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(54)【発明の名称】　感光性平版印刷版の処理方法

(57)【要約】

【課題】　露光後加熱を省略し、かつ耐刷性、汚れ性の改善された感光性平版印刷版の処理方法を提供する。

【解決手段】　中心線平均粗さ（Ｒａ）が０．３５μｍ以上の支持体上に、膜厚１．２～４ｇ／ｍ² の光重合性感光層及び膜厚２～８ｇ／ｍ² の保護層が順次積層されてなる感光性平版印刷版を、レーザー露光後、アルカリ金属珪酸塩を含有する現像液で現像し、その後、全面露光することを特徴とする感光性平版印刷版の処理方法。

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【特許請求の範囲】

【請求項１】　中心線平均粗さ（Ｒａ）が０．３５μｍ以上の支持体上に、膜厚１．２～４ｇ／ｍ² の光重合性感光層及び膜厚２～８ｇ／ｍ² の保護層が順次積層されてなる感光性平版印刷版を、レーザー露光後、アルカリ金属珪酸塩を含有する現像液で現像し、その後、全面露光することを特徴とする感光性平版印刷版の処理方法。

【請求項２】　光重合性感光層の膜厚が１．２～３．５ｇ／ｍ² である請求項１記載の感光性平版印刷版の処理方法。

【請求項３】　保護層の膜厚が２～７ｇ／ｍ² である請求項１又は２記載の感光性平版印刷版の処理方法。

【請求項４】　支持体が、硫酸を含む電解液を用いて陽＊

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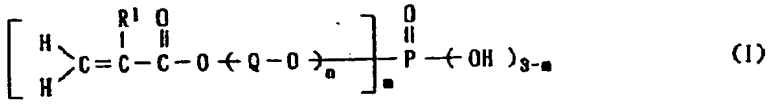
＊極酸化処理されたアルミニウム支持体であることを特徴とする請求項１乃至３記載の感光性平版印刷版の処理方法。

【請求項５】　光重合感光層が、少なくとも一つの（メタ）アクリロイル基を持つリン酸エステル化合物を含有することを特徴とする請求項１乃至４記載の感光性平版印刷版の処理方法。

【請求項６】　（メタ）アクリロイル基を持つリン酸エステル化合物が下記一般式（Ｉ）で表される化合物であることを特徴とする請求項５記載の感光性平版印刷版の処理方法。

【化１】



（Ｉ）

（一般式（Ｉ）中、Ｒ¹ は水素原子又はメチル基を示し、Ｑは炭素数１～２５の２価のアルキレン鎖を表わし、ｎは１～２の整数を示し、ｍは１又は２を示す。）

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明はレーザーによって露光を行う感光性平版印刷版の処理方法に関する。

【０００２】

【従来の技術】近年、コンピュータに入力し編集されたデジタルデータをレーザー走査線により直接感光性平版印刷版上に出力する製版システム（ＣＴＰシステム）が実用化の段階に進んできた。このシステムによる中間工程の省略によって、刷版作成工程の大幅な合理化が可能となった。ここに用いる版材としては取り扱いの簡便性や廃液の問題等から、光重合性感光材料を用いたフォトポリマー系の版材が有利である。しかしながら、フォトポリマー系感光材料は支持体との接着性が乏しいため、製版や印刷条件によっては耐刷力が極端に悪くなる問題があった。これを回避するため、処理プロセスの一環として、レーザー露光後１００℃程度の加熱処理工程を取り入れることがしばしば行なわれている。但し、この工程は機器を高温にする必要上夜間等の無人運転は難しく、また処理終了後も機器が有る程度冷却されるまでオペレーターが付いている必要があるため、ＣＴＰシステムの目的の一つである合理化と大きく逆行するものである。一方、フォトポリマー系版材を露光現像後、後露光することも知られている。

【０００３】

【発明が解決しようとする課題】しかしながら、本発明者の検討によれば後露光を行う場合でも版材の種類、現像液の種類によって、保存前後の耐刷性及び現像性（汚れ性）が不十分であることがわかった。即ち、本発明はフォトポリマー系の感光性平版印刷版に於て、露光後加熱を行うことなく、保存前後での安定した耐刷性及びその他の印刷性能の優れた印刷版を提供する処理方法を提供することにある。

【０００４】

【課題を解決するための手段】本発明者は鋭意検討を重ねた結果、特定の条件の感光性平版印刷版をレーザー露光、現像処理した後に全面露光することで上記課題が解決されることを見出した。即ち本発明の要旨は、中心線平均粗さ（Ｒａ）が０．３５μｍ以上の支持体上に、膜厚１．２～４ｇ／ｍ² の光重合性感光層及び膜厚２～８ｇ／ｍ² の保護層が順次積層されてなる感光性平版印刷版を、レーザー露光後、アルカリ金属珪酸塩を含有する現像液で現像し、その後、全面露光することを特徴とする感光性平版印刷版の処理方法に存する。

【０００５】

【発明の実施の形態】以下本発明について詳細に説明する。本発明の処理方法に用いる感光性平版印刷版は、親水性表面を有する支持体上に、光重合性感光性感光層及び酸素遮断層としての保護層を順次積層して成るものである。

【０００６】支持体としては、金属、プラスチック、紙等が用いられるが、特にアルミニウム支持体が好適に用いられる。支持体としてアルミニウム板を使用する場合、砂目立て処理、陽極酸化処理及び必要に応じて封孔処理等の表面処理が施される。これらの処理には公知の方法を適用することができる。

【０００７】砂目立て処理の方法としては、例えば、機械的方法、電解によりエッチングする方法が挙げられる。機械的方法としては、例えば、ボール研磨法、ブラシ研磨法、液体ホーミングによる研磨法、バフ研磨法等が挙げられる。電解エッチングは一般に酸性電解液中で

行なわれる。電解液としては塩酸又は硝酸を主体とするものが好ましく、また電解液には、必要に応じて塩化物、アミン類、アルデヒド類、リン酸、クロム酸、ホウ酸、酢酸、蓚酸等を加えることもできる。

【０００８】電解エッチングの条件は、電解液の種類により、選定されるが通常印加される電圧は１～５０Ｖ、好ましくは５～４０Ｖ、電流密度は１０～２００Ａ／ｄｍ²、好ましくは２０～１５０Ａ／ｄｍ² であり、使用される電流は交流、直流のどちらも使用できるが、交流電流の方がより好ましい。交流電流の周波数としては１～４００Ｈｚ、好ましくは２０～１００Ｈｚであり、電解液温度としては１０～５０℃、好ましくは１５～４０℃である。

【０００９】アルミニウム材の組成等に応じて上述の各種砂目立て方法を単独あるいは組み合わせて用いることが出来るが、この砂目立てによって生じる粗さはＪＩＳ規格による中心線平均粗さ（Ｒａ）で０．３５μｍ以上である必要がある。Ｒａがこれより小さい場合、充分な耐刷力の確保は難しい。Ｒａの上限は通常１．０μｍ以下である。電解エッチングの場合には、温度、時間、電圧、電流密度、電解液種、濃度等を適宜調節して、Ｒａを上記範囲とすることが可能である。電解粗面化されたアルミニウム支持体は、必要によりデスマット処理が行なわれる。デスマット処理は、酸またはアルカリの水溶液を使用する。上記の酸としては、例えば硫酸、硝酸、塩酸、リン酸、クロム酸等が含まれ、アルカリとしては、例えば水酸化ナトリウム、水酸化カリウム、第三リン酸カリウム、アルミン酸ナトリウム、メタ珪酸ナトリウム等が含まれるが、このなかでもアルカリを使用するのが好ましい。処理方式は上記の酸又はアルカリの水溶液に浸漬する方法や、スプレー方式等いかなる方式でも良い。上記をアルカリの水溶液で行った場合は、アルミニウム表面上にエッチング処理剤や、溶解されたスマット等の不純物が残留しているので、硫酸、硝酸、塩酸、リン酸、クロム酸等の酸、あるいはそれらの混酸による中和処理を行うことが好ましい。処理方式は浸漬、スプレー等いかなる方式でも良い。

【００１０】陽極酸化処理は、電解液として、硫酸、クロム酸、シュウ酸、リン酸、マロン酸等を１種又は２種以上含む溶液を用い、アルミニウム板を陽極として電解して行われる。陽極酸化処理条件は使用される電解液の種類によって変わるので一概に言えないが、例えば、硫酸および／または燐酸等の１～５０重量%の水溶液を電解液として、電解液温度５～７０℃、電流密度１～２０Ａ／ｄｍ² 、電圧１～１００Ｖ、電解時間１秒～５分である。他に、米国特許第１，４１２，７６８号明細書に記載されている硫酸中で高電流密度で電解する方法等を用いることができる。この中でも特に硫酸を含む電解液を用いたものが印刷時の汚れにくさや水巾の広さ等の点で最も優れている。尚、形成される陽極酸化皮膜量は１～５０ｍｇ／ｄｍ² が適当であり、好ましくは１０～４０ｍｇ／ｄｍ² である。

【００１１】陽極酸化処理後、必要により封孔処理を行なっても良い。封孔処理は、沸騰水処理、水蒸気処理、珪酸ソーダ処理、重クロム酸塩水溶液処理等が具体例として挙げられる。又、アルミニウム支持体に対して、カチオン性４級アンモニウム基を有する樹脂やポリビニルホスホン酸、澱粉、セルロース等の水溶性高分子化合物、フッ化ジルコン酸等の金属塩の水溶液による下引き処理を施すこともできる。

【００１２】本発明における感光性平版印刷版の光重合性感光層は、通常、高分子結合剤、エチレン性不飽和二重結合を少なくとも１個有する付加重合可能な化合物及び光重合開始剤を含有する光重合性組成物を上記処理を施した支持体上に塗布、乾燥して形成される。

【００１３】本発明において、エチレン性不飽和二重結合を少なくとも１個有する付加重合可能な化合物（以下「エチレン性化合物」と略す）とは、光重合性組成物が活性光線の照射を受けた場合、光重合開始剤の作用により付加重合し、硬化するようなエチレン性二重結合を有する化合物であって、例えばエチレン性不飽和二重結合を有する単量体、または、側鎖もしくは主鎖にエチレン性不飽和二重結合を有する重合体である。なお、本発明における単量体の意味するところは、いわゆる高分子物質に相対する概念である。従って、狭義の単量体以外に二量体、三量体、オリゴマーをも包含するものである。

【００１４】エチレン性不飽和二重結合を有する単量体としては、例えば不飽和カルボン酸；脂肪族ポリヒドロキシ化合物と不飽和カルボン酸とのエステル；芳香族ポリヒドロキシ化合物と不飽和カルボン酸とのエステル；不飽和カルボン酸と多価カルボン酸及び脂肪族ポリヒドロキシ化合物、芳香族ポリヒドロキシ化合物等の多価ヒドロキシ化合物とのエステル化反応により得られるエステル等が挙げられる。前記脂肪族ポリヒドロキシ化合物と不飽和カルボン酸とのエステルとしては、エチレングリコールジアクリレート、トリエチレングリコールジアクリレート、トリメチロールプロパントリアクリレート、トリメチロールエタントリアクリレート、ペンタエリスリトールジアクリレート、ペンタエリスリトールトリアクリレート、ペンタエリスリトールテトラアクリレート、ジペンタエリスリトールテトラアクリレート、ジペンタエリスリトールペンタアクリレート、ジペンタエリスリトールヘキサアクリレート、グリセロールアクリレート等のアクリル酸エステル、これら例示化合物のアクリレートをメタクリレートに代えたメタクリル酸エステル、同様にイタコネートに代えたイタコン酸エステル、クロトネートに代えたクロトン酸エステル、マレイネートに代えたマレイン酸エステル等がある。

【００１５】芳香族ポリヒドロキシ化合物と不飽和カルボン酸とのエステルとしては、ハイドロキノンジアクリ

レート、ハイドロキノンジメタクリレート、レゾルシンジアクリレート、レゾルシンジメタクリレート、ピロガロールトリアクリレート等が挙げられる。

【００１６】不飽和カルボン酸と多価カルボン酸および多価ヒドロキシ化合物とのエステル化反応により得られるエステルとしては必ずしも単一物ではないが代表的な具体例を挙げれば、アクリル酸、フタル酸及びエチレングリコールの縮合物；アクリル酸、マレイン酸及びジエチレングリコールの縮合物；メタクリル酸、テレフタル酸及びペンタエリスリトールの縮合物；アクリル酸、アジピン酸、ブタンジオール及びグリセリンの縮合物等がある。

【００１７】その他のエチレン性化合物の例としては、トリレンジイソシアネートとヒドロキシエチルアクリレートとの付加反応の様なウレタンアクリレート類；ジエポキシ化合物とヒドロキシエチルアクリレートとの付加反応の様なエポキシアクリレート類；エチレンビスアクリルアミド等のアクリルアミド類；フタル酸ジアクリル等のアクリル酸エステル類；ジビニルフタレート等のビニル基含有化合物などが有用である。

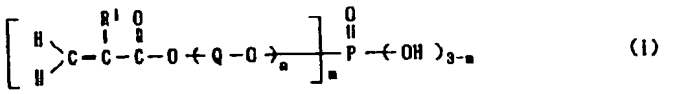
【００１８】前記した主鎖にエチレン性不飽和二重結合を有する重合体としては、例えば、不飽和二価カルボン酸とジヒドロキシ化合物との重縮合反応により得られるポリエステル、不飽和二価カルボン酸とジアミンとの重縮合反応により得られるポリアミド等がある。側鎖にエチレン性不飽和二重結合を有する重合体としては、側鎖に不飽和結合をもつ二価カルボン酸、例えばイタコン＊酸、プロヒリデンコハク酸、エチリデンマロン酸等とジヒドロキシまたはジアミン化合物等との縮合重合体がある。また、側鎖にヒドロキシ基やハロゲン化メチル基の如き反応活性を有する官能基を持つ重合体、例えばポリビニルアルコール、ポリ（２－ヒドキシエチルメタクリレート）、ポリエピクロルヒドリン等とアクリル酸、メタクリル酸、クロトン酸等の不飽和カルボン酸との高分子反応により得られるポリマーも好適に使用し得る。

【００１９】以上記載したエチレン性化合物の内、アクリル酸エステルまたはメタクリル酸エステルの単量体が特に好適に使用できる。更に、エチレン性化合物の内、上記以外のエチレン性不飽和二重結合を有する単量体として、少なくとも一つの（メタ）アクリロイル基を持つリン酸エステル化合物が挙げられ、これを含有した光重合性感光性組成物を用いた場合であって、特にこれを硫酸を含む電解液を用いて陽極酸化処理されたアルミニウム支持体と組み合わせた場合、本発明の効果はより顕著に発揮される。

【００２０】この少なくとも一つの（メタ）アクリロイル基を持つリン酸エステル化合物としては、リン酸エステルであって、その構造中に（メタ）アクリロイル基を少なくとも１つ有するものであれば特に限定されないがより具体的には、下記一般式（Ｉ）で表されるものが挙げられる。

【００２１】

【化２】



(I)

【００２２】（一般式（Ｉ）中、R^1 は水素原子又はメチル基を示し、Ｑは炭素数１～２５の２価のアルキレン鎖を表わし、ｎは１～２の整数を示し、ｍは１又は２を示す。）

式（Ｉ）に於て、好ましくはｎは１であり、更にＱが炭素数１～１０、特に１～４であるのが好ましい。該リン酸エステル化合物を含む場合、全エチレン性化合物中１～５０重量％が好ましい。

【００２３】次に光重合開始剤について説明する。光重合開始剤としては、前記エチレン性不飽和二重結合を少なくとも１個有する化合物の重合を開始させうるものはすべて使用できる。特に可視領域の光線に対して感光性を有するものであれば、いずれも好適に使用できる。この内、光励起された増感剤と何らかの作用を惹起することにより活性ラジカルを生成する活性剤としては、例えば、ヘキサアリールビイミダゾール類、チタノセン化合物、ハロゲン化炭化水素誘導体、ジアリールヨードニウム塩、有機過酸化物等を挙げることができる。この内、ヘキサアリールビイミダゾール類あるいは、チタノセン化合物を用いた系が、感度、保存性、塗膜の基板への密着性等が良く好ましい。

【００２４】ヘキサアリールビイミダゾール類としては、種々のものを用いることができるが、例えば、２，２’－ビス（ｏ－クロルフェニル）－４，４’，５，５’－テトラ（ｐ－フルオロフェニル）ビイミダゾール、２，２’－ビス（ｏ－ブロムフェニル）－４，４’，５，５’－テトラ（ｐ－ヨードフェニル）ビイミダゾール、２，２’－ビス（ｏ－クロルフェニル）－４，４’，５，５’－テトラ（ｐ－クロルナフチル）ビイミダゾール、２，２’－ビス（ｏ－クロルフェニル）－４，４’，５，５’－テトラ（ｐ－クロルフェニル）ビイミダゾール、２，２’－ビス（ｏ－ブロムフェニル）－４，４’，５，５’－テトラ（ｐ－クロル－ｐ－メトキシフェニル）ビイミダゾール、２，２’－ビス（ｏ－クロルフェニル）－４，４’，５，５’－テトラ（ｏ，ｐ－ジクロルフェニル）ビイミダゾール、２，２’－ビス（ｏ－クロルフェニル）－４，４’，５，５’－テトラ（ｏ，ｐ－ジブロムフェニル）ビイミダゾ

ール、２，２’－ビス（ｏ－ブロムフェニル）－４，４’，５，５’－テトラ（ｏ，ｐ－ジクロルフェニル）ビイミダゾール、２，２’－ビスｏ，ｐ－ジクロルフェニル）－４，４’，５，５’－テトラ（ｏ，ｐ－ジクロルフェニル）ビイミダゾール等が挙げられる。これらのビイミダゾールは、必要に応じ、他種のビイミダゾールと併用して使用することもできる。ビイミダゾール類は、例えばＢｕｌｌ．Ｃｈｅｍ．Ｓｏｃ．Ｊａｐａｎ，３３，５６５（１９６０）および　Ｊ．Ｏｒｇ．Ｃｈｅｍ，３６［１６］２２６２（１９７１）に開示されている方法により容易に合成することができる。

【００２５】チタノセン化合物としては、種々のものを用いることができるが、例えば、特開昭５９－１５２３９６号、特開昭６１－１５１１９７号各公報に記載されている各種チタノセン化合物から適宜選んで用いることができる。さらに具体的には、ジーシクロペンタジエニルーＴｉージークロライド、ジーシクロペンタジエニルーＴｉービスーフェニル、ジーシクロペンタジエニルーＴｉービスー２，３，４，５，６－ペンタフルオロフェニー１－イル、ジーシクロペンタジエニルーＴｉービスー２，３，５，６，－テトラフルオロフェニー１－イル、ジーシクロペンタジエニルーＴｉービスー２，４，６－トリフルオロフェニー１－イル、ジーシクロペンタジエニルーＴｉービスー２，６－ジーフルオロフェニー１－イル、ジーシクロペンタジエニルーＴｉービスー２，４－ジーフルオロフェニー１－イル、ジーメチルシクロペンタジエニルーＴｉービスー２，３，４，５，６－テトラフルオロフェニー１－イル、ジーメチルシクロペンタジエニルーＴｉービスー２，６－ジフルオロフェニー１－イル、ジーシクロペンタジエニルーＴｉービスー２，６－ジフルオロー３－（ピルー１－イル）－フェニー１－イル等を挙げることができる。

【００２６】次に、光重合開始剤の内の増感剤について説明する。本発明における増感剤とは、前述の活性剤と共存した場合、可視光線照射により、効果的に活性ラジカルを発生し得る化合物を意味している。代表的な増感剤の例としては、例えば、米国特許第３，４７９，１８５号明細書に開示されている様なロイコクリスタルバイオレットやロイコマラカイトグリーンの様なトリフェニルメタン系ロイコ色素、エリスロシンやエオシンＹの様な光還元性染料、米国特許第３，５４９，３６７号明細書、米国特許第３，６５２，２７５号明細書等に開示されているミヒラーズケトンやアミノスチリルケトンの様なアミノフェニルケトン類、米国特許第３，８４４，７９０号明細書に示されるβ－ジケトン類、米国特許第４，１６２，１６２号明細書に見られるインダノン類、特開昭５２－１１２６８１号公報に示されるケトクマリン類、特開昭５９－５６４０３号公報で開示されているアミノスチレン誘導体やアミノフェニルブタジエン誘導体、米国特許第４，５９４，３１０号明細書に見られるアミノフェニル複素環類、米国特許第４，９６６，８３０号明細書に示されるジュロリジン複素環類、特開平５－２４１３３８号公報に示されるピロメテン系色素などが挙げられる。

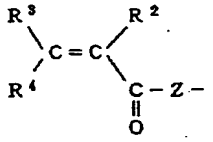
【００２７】さらに、本発明で用いる光重合開始剤に必要に応じて２－メルカプトベンゾチアゾール、２－メルカプトベンズイミダゾール、２－メルカプトベンズオキサゾール、３－メルカプト１，２，４－トリアゾール、Ｎ－フェニルグリシン、Ｎ，Ｎ－ジアルキル安息香酸アルキルエステル等の水素供与性化合物を加えることによってさらに光重合開始能力を高めることができる。このうち特に好ましいのは、２－メルカプトベンゾチアゾール、２－メルカプトベンズイミダゾール、２－メルカプトベンズオキサゾール、３－メルカプト１，２，４－トリアゾール等のメルカプト基を有する化合物である。

【００２８】次に高分子結合剤について説明する。これは、皮膜形成能や粘度調節能を付与する成分であり、アルカリ可溶性の高分子結合剤、中でも分子内にカルボキシル基を有する高分子結合剤が好ましく用いられる。分子内にカルボキシル基を有する高分子結合剤の具体例としては、例えば、（メタ）アクリル酸、（メタ）アクリル酸エステル、（メタ）アクリルアミド、マレイン酸、（メタ）アクリロニトリル、スチレン、酢酸ビニル、塩化ビニリデン、マレイミド等の単独もしくは共重合体、その他、ポリエチレンオキサイド、ポリビニルピロリドン、ポリアミド、ポリウレタン、ポリエステル、ポリエーテル、ポリエチレンテレフタレート、アセチルセルロース、またはポリビニルブチラール等が挙げられる。中でも（メタ）アクリル酸エステルの少なくとも一種と（メタ）アクリル酸を共重合成分として含有する共重合体が好ましい。分子内にカルボキシル基を有する高分子結合剤の好ましい酸価の値は１０～２５０であり、好ましい重量平均分子量（以下Ｍｗと略す）は５千から５０万である。

【００２９】これらの高分子結合剤は、側鎖に不飽和結合を有する事が望ましく、特に下記一般式（II）で示される少なくとも１種の不飽和結合を有する事が好ましい。

【００３０】

【化３】



（II）

【００３１】（式中、R^2 は水素原子又はメチル基を示す。また、R^3 ～R^4 は各々独立して水素原子、ハロゲン原子、アミノ基、ジアルキルアミノ基、カルボキシル基、アルコキシカルボニル基、スルホ基、ニトロ基、シ

アノ基、置換基を有していてもよいアルキル基、置換基を有していてもよいアリール基、置換基を有していてもよいアルコキシ基、置換基を有していてもよいアリールオキシ基、置換基を有していてもよいアルキルアミノ基、置換基を有していてもよいアリールアミノ基、置換基を有していてもよいアルキルスルホニル基、又は置換基を有していてもよいアリールスルホニル基を示し、Ｚは酸素原子、硫黄原子、イミノ基、又はアルキルイミノ基を示す。）

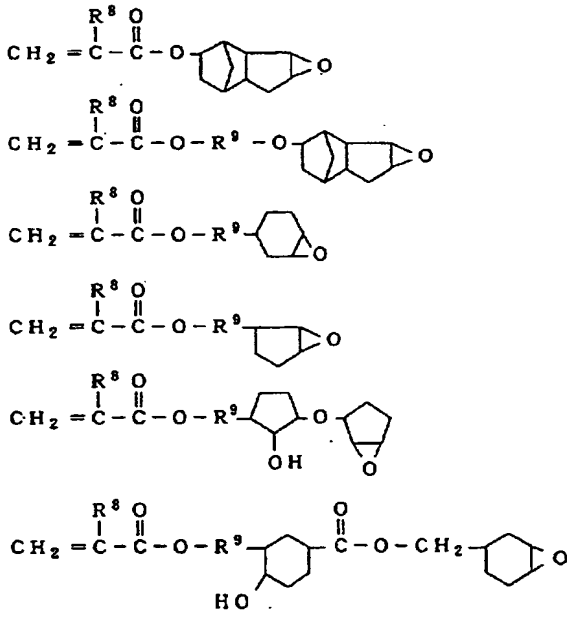
【００３２】なお、置換基を有していても良いアルキル基等の置換基としては炭素－炭素二重結合の反応性を極端に低下させない限り特に限定されないが、通常ハロゲン原子、アルキル基、フェニル基、シアノ基、ニトロ基、アルコキシ基、アルキルチオ基、又はジアルキルアミノ基等から選ばれる。これらの内、R^2 が水素原子又はメチル基であり、R^3 及びR^4 が各々独立して水素原子、低級アルキル基、アルコキシ基、ジアルキルアミノ基、又はシアノ基であるものが更に好ましい。

＊【００３３】分子内にカルボキシル基を含有し、更に側鎖に不飽和結合を有する高分子結合剤としては、特願平９－３４６１４４号に記載の如き、分子内にカルボキシル基を有する高分子結合剤のカルボキシル基の一部をエポキシ基含有不飽和化合物と反応させた化合物が挙げられる。

【００３４】エポキシ基含有不飽和化合物としては、グリシジル（メタ）アクリレート、アリルグリシジルエーテル、α－エチルグリシジルアクリレート、クロトニルグリシジルエーテル、グリシジルクロトネート、グリシジルアソクロトネート、イタコン酸モノアルキルエステルモノグリシジルエステル、フマール酸モノアルキルエステルモノグリシジルエステル、マレイン酸モノアルキルエステルモノグリシジルエステル等の脂肪族エポキシ基含有不飽和化合物および下記構造で示される脂環式エポキシ基含有不飽和化合物が挙げられる。

【００３５】

＊【化４】



【００３６】（各一般式中、R^8 は水素原子又はメチル基を示す。R^9 は炭素数１～６の２価の脂肪族飽和炭化水素基を示す。）

以上、感光層を形成する光重合性組成物の主要構成成分について詳述してきたが、それらの好適な使用比率は、エチレン性化合物１００重量部に対して光重合開始剤の内、増感剤が好ましくは０．０１～２０重量部、特に好ましくは０．０５～１０重量部、活性剤が好ましくは０．１～８０重量部、特に好ましくは０．５～５０重量部、高分子結合剤が、好ましくは１０～４００重量部、特に好ましくは２０～２００重量部の範囲である。

【００３７】尚、光重合性組成物は前記の各構成成分の他に、それの使用目的に応じて、更に他の物質を添加混合することができる。例えば、ハイドロキノン、ｐ－メトキシフェノール、２，６－ジ－ｔ－ブチル－ｐ－クレゾールなどの熱重合防止剤；有機または無機の染顔料からなる着色剤；ジオクチルフタレート、ジドデシルフタレート、トリクレジルホスフェート等の可塑剤、三級アミンやチオールの様な感度特性改善剤、その他色素前駆体などの添加剤も加えることができる。

【００３８】以上述べた各種添加剤の好ましい添加量は、エチレン性化合物１００重量部に対して熱重合防止

剤２重量部以下、着色剤２０重量部以下、可塑剤４０重量部以下、色素前駆体３０重量部以下の範囲であることが一般的である。以上述べた光重合性組成物は、適当な溶媒で希釈して、前記支持体上に塗布、乾燥し感光層として塗設される。塗布方法としては、ディップコート、コーティグロッド、スピナーコート、スプレーコート、ロールコート等の周知の方法により塗布することが可能である。塗布膜厚は、乾燥膜厚として１．２～４ｇ／ｍ²である必要があり、これより薄い場合は保存性が悪化（感度低下、現像時抜け不良）し、厚い場合は感度不足となり、本発明の効果が充分に発揮されない。好ましくは１．２～３．５ｇ／ｍ²である。乾燥温度は、好ましくは３０～１５０℃、特に好ましくは４０～１１０℃である。

【００３９】本発明の感光性平版印刷版における光重合性感光層の上層には、酸素による重合禁止作用を防止するための酸素遮断層として、保護層を設ける。保護層は通常水溶性高分子結合剤を含有し、公知の種々の水溶性高分子化合物が挙げられるが、具体例としてはポリビニルアルコール、ポリビニルピロリドン、ポリエチレンオキサイド、セルロース等の水溶性高分子化合物が挙げられる。水溶性高分子化合物の重量平均分子量は１０００～３０万程度である。この内、特に酸素ガスバリア性の高いポリビニルアルコールを用いたものが好ましい。

【００４０】これら水溶性高分子は単独または混合で用い、また感光層への塗布性を向上させる目的等で界面活性剤の添加が好適に行われる。塗布方法としては、感光層と同様に周知の塗布方法により塗布することが可能である。塗布膜厚は、乾燥膜厚として２～７ｇ／ｍ²である必要があり、これより薄い場合は感度が不充分であり、厚い場合は保存性が悪化し、感度低下による現像時抜け不良が発生し本発明の効果が充分に発揮されない。乾燥温度は、３０～１１０℃であることが一般的であり、好ましくは４０～７０℃である。

【００４１】本発明で用いる現像液は、アルカリ金属珪酸塩を含有する水溶液である。アルカリ金属珪酸塩としては、珪酸カリウム、珪酸ナトリウム、珪酸リチウム、メタ珪酸カリウム、メタ珪酸ナトリウム等があり、この他水酸化カリウム、水酸化ナトリウム、水酸化リチウム、第三リン酸ナトリウム、第二リン酸ナトリウム、炭酸ナトリウム、炭酸カリウム、重炭酸ナトリウム等の無機アルカリ剤、及びトリメチルアミン、ジエチルアミン、イソプロピルアミン、ｎ－ブチルアミン、モノエタノールアミン、ジエタノールアミン、トリエタノールアミン類等の有機アミン化合物などのアルカリ剤を併用しても良い。

【００４２】本発明の現像液には更に界面活性剤を含有することが好ましい。本発明の現像液に用いられる界面活性剤としては、例えば、ポリオキシエチレンラウリルエーテル、ポリオキシエチレンセチルエーテル、ポリオキシエチレンステアリルエーテル等のポリオキシエチレンアルキルエーテル類、ポリオキシエ」チレンオクチルフェニルエーテル、ポリオキシエチレンノニルフェニルエーテル等のポリオキシエチレンアルキルアリルエーテル類、ポリオキシエチレンステアレート等のポリオキシエチレンアルキルエステル類、ソルビタンモノラウレート、ソルビタンモノステアレート、ソルビタンジステアレート、ソルビタンモノオレエート、ソルビタンセスキオレエート、ソルビタントリオレエート等のソルビタンアルキルエステル類、グリセロールモノステアレート、グリセロールモノオレート等のモノグリセリドアルキルエステル類等のノニオン界面活性剤；ドデシルベンゼンスルホン酸ナトリウム等のアルキルベンゼンスルホン酸塩類、ブチルナフタレンスルホン酸ナトリウム、ペンチルナフタレンスルホン酸ナトリウム、ヘキシルナフタレンスルホン酸ナトリウム、オクチルナフタレンスルホン酸ナトリウム等のアルキルナフタレンスルホン酸塩類、ラウリル硫酸ナトりウム等のアルキル硫酸塩類、ドデシルスルホン酸ソーダ等のアルキルスルホン酸塩類、ジラウリルスルホコハク酸ナトリウム等のスルホコハク酸エステル塩類等のアニオン界面活性剤；ラウリルベタイン、ステアリルベタイン等のアルキルベタイン類、アミノ酸類等の両性界面活性剤が使用可能であるが、特に好ましいのはアルキルナフタレンスルホン酸塩類等のアニオン界面活性剤である。

【００４３】これら界面活性剤は単独、もしくは組み合わせて使用することが出来る。また、これら界面活性剤の現像液中における含有量は有効成分換算で０．１から５重量%が好ましい。尚、本発明で言う現像液とは現像のスタート時に使用される未使用の液だけでなく、ＰＳ版の処理によって低下する液の活性度を補正するために補充液が補充され、活性度が保たれた液（いわゆるランニング液）を含む。

【００４４】また、本発明で言う現像液とは実際にＰＳ版の処理をする状態にあるものを指す。本発明の現像液には上記の成分の他に、必要に応じて以下の様な成分を併用することができる。例えば安息香酸、フタル酸、p-エチル安息香酸、p-n-プロピル安息香酸、p-イソプロピル安息香酸、p-n-ブチル安息香酸、p-t-ブチル安息香酸、p-t-ブチル安息香酸、p-2-ヒドロキシエチル安息香酸、デカン酸、サリチル酸、３－ヒドロキシ－２－ナフトエ酸等の有機カルボン酸；イソプロピルアルコール、ベンジルアルコール、エチルセロソルブ、ブチルセロソルブ、フェニルセロソルブ、プロピレングリコール、ジアセトンアルコール等の有機溶剤；この他、キレート剤、還元剤、染料、顔料、硬水軟化剤、防腐剤等が挙げられる。

【００４５】本発明の処理方法で用いる露光光源はレーザーであり、具体的にはヘリウムカドミウムレーザー、アルゴンイオンレーザー、ＹＡＧレーザー、ヘリウムネ

オンレーザー等が挙げられる。本発明の処理法方ではレーザー露光後、加熱処理することなく前述の現像液により現像される。現像は、ディップ現像、スプレー現像等、公知の方法により行なわれる。

【００４６】本発明の処理方法では、この現像処理後、さらに全面露光（後露光）を行うことを特徴としており、その光源としては特に限定はされないが例えば、カーボンアーク、高圧水銀灯、キセノンランプ、メタルハライドランプ、蛍光ランプ、タングステンランプ、ハロゲンランプ等が挙げられる。これらの光源から発せられる光はフィルター等によって波長制限して用いる場合もあり得る。また、その後露光量は特に限定するものでは無く、大きい程効果は期待出来るが、刷版工程の合理化という意味から１０ｍＪ／ｃｍ² 以上１０００ｍＪ／ｃｍ² 以下が好ましい。

【００４７】

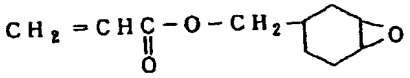
【実施例】以下、本発明を実施例により更に具体的に説明するが、本発明はこれら実施例により限定されるものではない。

【００４８】高分子結合剤－１の合成

メチルメタクリレート／イソブチルメタクリレート／イソブチルアクリレート／メタアクリル酸＝３５／２０／１０／３５ｍｏｌ％（仕込み比）の共重合体、Ｍｗ＝７万（以下「幹樹脂－１」と略す。）を２００重量部、下記脂環式エポキシ基含有不飽和化合物７５重量部、ｐ－メトキシフェノール２．５重量部、テトラブチルアンモニウムクロライド８重量部、プロピレングリコールモノメチルエーテルアセテート８００重量部を反応容器に中に加え、１１０℃、２４時間空気中で撹拌反応させて高分子結合剤－１（酸化６０、幹樹脂－１のメタアクリル酸成分全体の６割に不飽和基が反応）溶液を得た。

【００４９】

【化５】

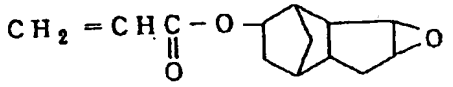


【００５０】高分子結合剤－２の合成

α－メチルスチレン／アクリル酸の共重合体（商品名“ＳＣＸ－６９０”Ｊｏｈｎｓｏｎ社製、酸化２４０、Ｍｗ＝１．５万）を８５５重量部、下記脂環式エポキシ含有不飽和化合物４９０重量部、ｐ－メトキシフェノール１．３重量部、テトラエチルアンモニウムクロライド４．３重量部、プロピレングリコールモノメチルエーテルアセテート１８００重量部を反応容器中に加え、１２０℃、１５時間空気中で撹拌反応させて高分子結合剤－２（酸化約１７０、ＳＣＸ－６９０のメタアクリル酸成分全体の約５割に不飽和基が反応）溶液を得た。

【００５１】

【化６】



【００５２】支持体－１

アルミニウム版を３％水酸化ナトリウムにて脱脂し、これを１８．０ｇ／ｌ硝酸浴中で２５℃、８０Ａ／ｄｍ² の電流密度で１５秒間エッチングし、その後５０℃の１％水酸化ナトリウム水溶液で５秒間デスマット処理を行い、次に２５℃の１０％硝酸水溶液で５秒間中和した。水洗後３０％硫酸浴中で３０℃、１０Ａ／ｄｍ² の条件で１６秒間陽極酸化し、水洗、乾燥してＲａが０．５５μｍの支持体－１を得た。

【００５３】支持体－２

アルミニウム版を３％水酸化ナトリウムにて脱脂し、これを１１．５ｇ／ｌ塩酸浴中で２５℃、８０Ａ／ｄｍ² の電流密度で１１秒間エッチングし、その後５０℃の１％水酸化ナトリウム水溶液で５秒間デスマット処理を行い、次に２５℃の１０％硝酸水溶液で５秒間中和した。水洗後３０％硫酸浴中で３０℃、１０Ａ／ｄｍ² の条件で１６秒間陽極酸化し、水洗、乾燥してＲａが０．６３μｍの支持体－２を得た。

【００５４】支持体－３（比較支持体）

支持体－１の方法に於て、硝酸浴中でのエッチング条件を電流密度４０Ａ／ｄｍ² 、エッチング時間５秒間に変更した以外同様にしてＲａが０．３μｍの支持体－３を得た。

【００５５】感光性平版印刷版－１～９の製造

上記支持体－１、２又は３に下記光重合性組成物塗布液をバーコーターを用いて塗布乾燥した。更にこの上に、ポリビニルアルコール水溶液を塗布乾燥して保護膜を形成し、感光性平版印刷版－１～９を作成した。尚、それぞれの乾燥膜厚は表－１に示した。

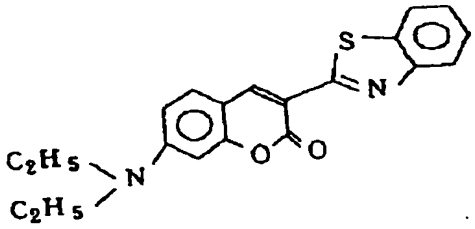
【００５６】

光重合性組成物塗布液

表－１に示すエチレン性単量体	合計　５５	重量部
表－１に示す高分子結合剤	４５	重量部
下記構造（Ａ）の化合物	２．０	重量部
下記構造（Ｂ）のチタノセン化合物	１０	重量部
２－メルカプトベンゾチアゾール	５．０	重量部
Ｎ，Ｎ－ジメチル安息香酸エチルエステル	１０	重量部
銅フタロシアニン顔料	３．０	重量部
シクロヘキサノン	１０９０	重量部

【００５７】

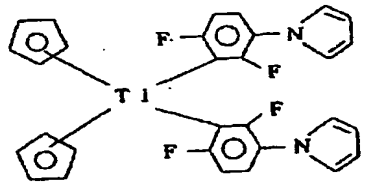
＊　＊【化７】



（Ａ）

【００５８】

【化８】



（Ｂ）

【００５９】

【表１】

表－１

		感光性平版印刷版								
		1	2	3	4	5	6	7	8	9
エチレン性単量体（重量部）	1	5	5	5	5	5	5	10	10	10
	2	25	25	25	25	25	25	23	23	23
	3	25	25	25	25	25	25	23	23	23
高分子結合剤（重量部）	1	40	40	40	40	40	40	34	34	34
	2	5	5	5	5	5	5	10	10	10
支持体		1	1	1	2	3	3	1	1	1
感光層膜厚（g/m²）		2	1	2	2	2	1	2	5	2
保護層膜厚（g/m²）		3	3	8	3	3	3	4	4	1

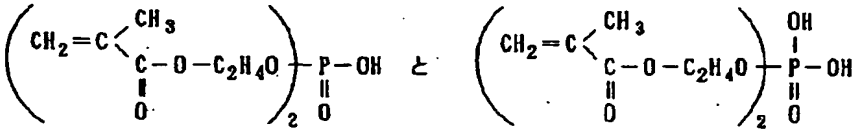
【００６０】表－１におけるエチレン性単量体の欄の略号はそれぞれ下記のものを示す。

１：日本化薬（株）社製　　ＰＭ－２

★【００６１】

【化９】

★

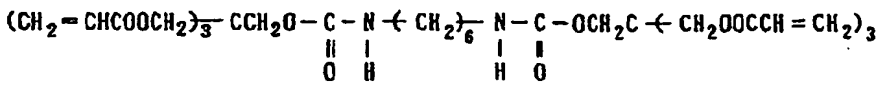


のｉ：１（モル比）混合物

２：新中村化学（株）社製　　ＵＡ－３０６Ｈ

【化１０】

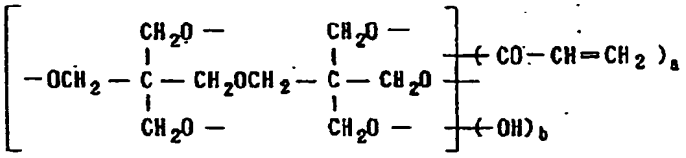
【００６２】



3：日本化薬（株）社製　　ＤＰＨＡ　　＊【化１１】

【００６３】

＊



ａ＝６，ｂ＝０　と　ａ＝５，ｂ＝１

【００６４】（実施例－１～７、比較例－１～６）上記の感光性平版印刷版１～９を、アルゴンレーザー（光量１３０μＪ／ｃｍ²、波長４８８ｎｍ）で内面ドラム式の走査露光を行った。上記の様に露光処理した感光性平版印刷版－１～９を自動現像機ＨＬ－８６０Ｘ（三菱化学（株）製）を用いて、表－２に示した現像液で現像処理を行った。尚、現像液温は３０℃、搬送速度は６０ｃｍ／分で行った。

【００６５】その後、上記印刷版の一部は表－２に従って水銀灯（１５０ｍＪ／ｃｍ²）で後露光処理を行った。得られた印刷版を印刷機（ローランドＲＰ－１）に※かけ耐刷テストを行った。耐刷性は、１０万枚印刷後の画像部の２％小点の状態で判定した（○：８０％以上再現、×：再現率８０％未満）。

【００６６】さらに、感光性平版印刷版－１～９を作成後、半年経過した時点で同様の製版を行い、耐刷テストを行った。また、その際、強制的に湿し水を絞り全面を汚した後水を再供給し、汚れが回復するまでに要した印刷枚数で汚れ性を評価した（○：２０枚未満、×：２０枚以上）。

【００６７】

【表２】

表－２

	感光性平版（備考）	現像液	後露光	耐刷性	半年後耐刷性	汚れ性（備考）
実施例－１	１	１	有り	○	○	○
比較例－１	１	１	無し	×	×	○
比較例－２	１	２(Si無)	有り	○	○	×
比較例－３	２（感光層薄膜）	１	有り	○	×	×（現像性も悪化）
比較例－４	２（感光層薄膜）	１	無し	×	×	×（現像性も悪化）
比較例－５	３（保護層厚膜）	１	有り	○	×	×（現像性も悪化）
実施例－２	４	１	有り	○	○	○
比較例－６	４	１	無し	×	×	○
比較例－７	４	２(Si無)	有り	○	○	×
比較例－８	５（Ｒａ小）	１	有り	×	×	○
比較例－９	６（Ｒａ小）	１	有り	×	×	○
実施例－３	７	１	有り	○	○	○
比較例－10	７	１	無し	×	×	○
比較例－11	８（感光層厚膜）	１	有り	×	×	○
比較例－12	９（保護層薄膜）	１	有り	×	×	○

【００６８】

＊現像液－１（ｐＨ＝１０．８）

珪酸カリウム（ＪＩＳ　Ａ珪酸カリ）	３重量％
ペレックスＮＢＬ（花王（株）製）	５重量％
（アルキルナフタレンスルフォン酸ナトリウム；含有率３５％）	
水	９２重量％

現像液－２（ｐＨ＝１１．０）

炭酸ナトリウム	０．５重量％
ペレックスＮＢＬ（花王（株）製）	５重量％
（アルキルナフタレンスルフォン酸ナトリウム；含有率３５％）	
水	９４．２重量％

【００６９】

【発明の効果】本発明によれば、露光後加熱を省略することが可能であるためＣＴＰ化による刷版作成工程の合理性を損なうことなく、しかも保存後の耐刷性、汚れ性が良好で安定した印刷性能の確保が可能となる。

Our Ref.: MC-671 (A-0056)

TITLE OF THE INVENTION

METHOD FOR TREATING PHOTOSENSITIVE LITHOGRAPHIC PRINTING PLATE

TECHNICAL FIELD

The present invention relates to a method for treating a photosensitive lithographic printing plate for exposure by laser.

PRIOR ARTS

In recent years, a printing plate making system (CTP system) which comprises outputting digital data inputted into a computer and edited, directly on a photosensitive lithographic printing plate by laser scanning lines, has been developed to be practically usable. By this step, a large rationalization of a printing plate making step has become possible. As a photosensitive lithographic printing plate used for this system, a photopolymer type photosensitive lithographic printing plate using a photopolymerizable photosensitive material is useful from viewpoints of easy handling, a problem of a waste water, and the like. However, since a photopolymer type photosensitive material is poor in adhesiveness with a support, there has been a problem that a printing resistance becomes extremely poor depending on plate making and printing conditions. In order avoid these problems, a heat-treating step at about 100°C is often carried out after subjecting a photosensitive

lithographic printing plate to laser exposure as one step of printing plate making process. However, since this heat-treating step requires to maintain an apparatus at a high temperature, it is difficult to carry out unmanned operation even during night time and the apparatus must accompanied by an operator even after treatment until it is cooled to a certain level. This makes an obstacle to the above-mentioned rationalization which is one of objects of CTP system. On the other hand, it is known to carry out post-exposure after exposing a photopolymer type photosensitive lithographic printing plate to laser light and developing.

For example, JP-A-6-148885 and JP-A-6-289611 provide a photopolymerizable composition having a satisfactory developing property and a high resolving power by containing a specific photopolymerization initiator, and their examples illustrate steps of exposing a photopolymerizable photosensitive lithographic printing plate to laser light, developing with a sodium carbonate aqueous solution and then carrying out post-exposure by a metal halide lamp. More concretely, it is disclosed (1) to prepare a photosensitive lithographic printing plate by forming an overcoat layer of a dry thickness of 1.5 g/m^2 for shielding an enzyme after forming a photopolymerizable photosensitive layer of a dry weight of 3.5 g/m^2 on an aluminum plate of 0.6 μm having a surface roughness of Ra after surface-roughening

treatment, (2) to describe a pattern on said photosensitive lithographic printing plate by scanning exposure with an argon ion laser of 1 mJ/cm^2, and then (3) to carry out post-exposure with a metal halide lamp of 1 J/cm^2 to complete a printing plate.

However, according to the analysis by the present inventors, it has been found that even in the case of carrying out post-exposure, depending on a kind of photosensitive lithographic printing plate and a kind of a developer, a printing resistance and a developing property (stain property) before and after storing are unsatisfactory. Thus, the present invention provides a method for treating a photosensitive lithographic printing plate to provide a photopolymer type photosensitive lithographic printing plate having a stable printing resistance and excellent in other printing performances before and after storing.

On the other hand, an effect of improving an image strength achieved by carrying out post-exposure after development can be expected to some extent since a total light exposure amount imparted to a formed image becomes large. Heretofore, a total light exposure amount was seriously considered, but a light intensity (light exposure amount per unit time) on a surface to be exposed was not seriously considered. Also, in view of a general relation between a light intensity of a post-exposure light source and a distance from the light source to a

surface to be exposed, the light intensity on the surface to be exposed was considered to be relatively low, usually at most about 15 mW/cm^2, and such an image strength as to satisfy a commercial demand could not be achieved even by post-exposure treatment.

Thus, an object of the present invention is to provide a method for treating a photosensitive lithographic printing plate, which gives a satisfactory image strength to an image obtained by laser light scanning exposure and development and reduces a required light exposure amount at the time of laser light exposure.

DISCLOSURE OF THE INVENTION

The present inventors have conducted an extensive study and have found that the above problems can be solved by exposing a photosensitive lithographic printing plate having specific conditions to laser light, developing with a specific developer and then carrying out post-exposure treatment.

That is, the first essential feature of the present invention resides in a method for treating a photosensitive lithographic printing plate, which comprises exposing the photosensitive lithographic printing plate to laser light, developing with a developer containing an alkali metal silicate and then carrying out post-exposure treatment, said photosensitive lithographic printing plate being prepared by forming a photopolymerizable photosensitive layer having a film

thickness of from 1.2 to 4 g/m^2 and further forming a protective layer having a film thickness of from 2 to 8 g/m^2 on a support having a centerline average height (Ra) of at least 0.35 μm.

Further, the present inventors have conducted an extensive study to solve the above problems, and have found that the above objects can be achieved by defining a light intensity on an image-forming surface in a specific range at the time of carrying out the post-exposure treatment. That is, the second essential feature of the present invention resides in a method for treating a photosensitive lithographic printing plate, which comprises exposing the photosensitive lithographic printing plate to laser light, developing and then carrying out post-exposure treatment at a light intensity of from 20 to 500 mW/cm^2 on a surface to be exposed at the time of the post-exposure treatment, said photosensitive lithographic printing plate being prepared by forming a photosensitive layer comprising a photopolymerizable composition containing an ethylenic compound, a photopolymerization initiator and a high molecular binder on the surface of a support.

Preferably, the post-exposure treatment of each of the above methods is carried out by a mercury lamp.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

Hereinafter, the present invention is described in details.

A photosensitive lithographic printing plate used in the method of the present invention is prepared by forming a photopolymerizable photosensitive layer and a protective layer as an oxygen-shielding layer in order on a support having a hydrophilic surface.

Examples of the support include metal, plastic, paper and the like, and an aluminum support is particularly preferably used. When an aluminum plate is used as the support, it is subjected to surface treatments including roughening treatment (sand blasting), anodization and optionally sealing treatment. These treatments can be carried out by well known methods.

Examples of the roughening treatment include a mechanical method, an etching method by electrolysis and the like. Examples of the mechanical method include ball abrading method, brush abrading method, hydro-honing abrading method, buff abrading method and the like. The hydrolysis etching is generally carried out in an acidic hydrolyte. The hydrolyte comprises preferably hydrochloric acid or nitric acid as the main component, and an acid concentration is usually from 0.5 to 5 wt%. Also, the hydrolyte may optionally contain further a chloride, amines, aldehydes, phosphoric acid, chromic acid, boric acid, acetic acid, oxalic acid and the like, if necessary.

Conditions of the electrolytic etching are selected depending on a kind of an electrolyte used, but a voltage

applied is usually from 1 to 50 V, preferably from 5 to 40 V, and an electric current density is from 10 to 200 A/dm^2, preferably from 20 to 150 A/dm^2. The electric current used may be either direct current or alternating current, but alternating current is preferable. The frequency of the alternating current is from 1 to 400 Hz, preferably from 2 to 100 Hz, and the electrolyte temperature is from 10 to 50°C, preferably from 15 to 40°C.

Depending on a composition or other conditions of an aluminum material used, the above-mentioned various surface roughening methods can be used respectively alone or in combination, but a roughness produced by this roughening treatment is required to be a centerline average height (Ra) of at least 0.35 μm in terms of JIS standard. If Ra is smaller than the above value, a satisfactory printing resistance can hardly be obtained. The upper limit of Ra is usually at most 1.0 μm. In the case of electrolytic etching, it is possible to maintain a Ra value within the above-mentioned range by optionally controlling temperature, time, voltage, electric current density, a kind of electrolyte, concentration or the like. The electrolytically roughened aluminum support may optionally be subjected to desmut treatment, if necessary. The desmut treatment is carried out by using an acid or alkali aqueous solution. Examples of the acid include sulfuric acid, nitric acid, hydrochloric acid, phosphoric

acid, chromic acid and the like, and examples of the alkali include sodium hydroxide, potassium hydroxide, potassium tertiary phosphate, sodium aluminate, sodium metasilicate, and the like. Among them, it is preferable to use alkali . Examples of treatment system include a method of dipping in the above acid or alkali aqueous solution, a spraying method and the like. When the desmut treatment is carried out by using an alkali aqueous solution, it is preferable to carry out neutralization treatment with an acid such as sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, chromic acid or the like or a mixed acid thereof since an etching treating agent or impurities including dissolved smut remain on the aluminum surface. This treatment system may be any type of system such as dipping or spraying.

Anodization treatment is carried out by electrolysis using an aluminum plate as an anode and using one or two or more solutions of sulfuric acid, chromic acid, oxalic acid, phosphoric acid, malonic acid or the like as an electrolyte. Conditions of the anodization treatment vary depending on a kind of an electrolyte used, but an aqueous solution comprising from 1 to 50 wt%, preferably from 15 to 30 wt%, of sulfuric acid and/or phosphoric acid is used as an electrolyte under conditions of an electrolyte temperature of from 5 to 70°C, preferably from 15 to 35°C, an electric current density of from 1 to

20 A/dm^2, an electric voltage of from 1 to 100 V and an electrolysis time of from 1 second to 5 minutes. Further, as described in U.S. Patent No. 1,412,768, a method of electrolyzing in sulfuric acid at a high electric current density may be used. Among them, a method of using an electrolyte containing sulfuric acid is particularly preferable in respect that a printing plate is hardly stained at the time of printing and a width (damping water width) of an amount of damping water applied onto a printing plate at the time of printing is large. Also, an amount of an anodized film formed is suitably from 1 to 50 mg/dm^2, preferably from 10 to 40 mg/dm^2.

After anodizing treatment, sealing treatment may be carried out, if necessary. Examples of the sealing treatment include treatment with boiling water, treatment with water vapor, treatment with sodium silicate, treatment with bichromate aqueous solution, and the like. Also, an aluminum support may optionally be subjected to undercoating treatment with a water soluble high molecular compound such as cellulose, starch, polyvinyl phosphonic acid or a resin having a cationic quaternary ammonium group, or an aqueous solution of a metal salt of fluorozirconic acid.

The photopolymerizable photosensitive layer of the photosensitive lithographic printing plate of the present invention is usually formed by coating a photopolymerizable composition containing a high

molecular binder, an addition-polymerizable compound having at least one ethylenic unsaturated double bond and a photopolymerization initiator on the above treated support and drying.

The addition-polymerizable compound having at least one ethylenic unsaturated double bond (hereinafter referred to as "ethylenic compound") used in the present invention means a compound having an ethylenic double bond addition-polymerizable by the action of a photopolymerization initiator and curable when the photopolymerizable composition is irradiated with an active light, for example, a monomer having an ethylenic unsaturated double bond. The term "monomer" used in the present invention means a material opposed to a high molecular material, and includes a dimer, a trimer and an oligomer, in addition to a monomer.

In the present invention, an ethylenic compound may be a compound having one ethylenic unsaturated bond in a molecule, such as an unsaturated carboxylic acid including (meth)acrylic acid (the term "(meth)acryl" used in the present invention means "acryl" and "methacryl"), crotonic acid, isocrotonic acid, maleic acid, itaconic acid, citraconic acid or the like, and their alkyl esters, (meth)acrylonitrile, (meth)acrylamide, styrene and the like, but a compound having at least two ethylenic unsaturated bonds in a molecule is preferable.

Examples of such an ethylenic compound include an

unsaturated carboxylic acid; an ester of an aliphatic polyhydroxy compound and an unsaturated carboxylic acid; an ester of an aromatic polyhydroxy compound and an unsaturated carboxylic acid; an ester obtained by esterification of an unsaturated carboxylic acid and a polyhydroxy compound such as a polyhydric carboxylic acid, an aliphatic polyhydroxy compound, an aromatic polyhydroxy compound or the like, urethane(meth)acrylates obtained by reaction of a polyisocyanate compound and a hydroxy(meth)acrylate compound, epoxy(meth)acrylates obtained by reaction of a polyepoxy compound and a (meth)acrylic acid or hydroxy(meth)acrylate compound, and a (meth)acryloyl group-containing phosphoric acid ester compound, and the like.

Examples of said ester of an aliphatic polyhydroxy compound and an unsaturated carboxylic acid include reaction products of said unsaturated carboxylic acid and said aliphatic polyhydroxy compound such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, tripropylene glycol, trimethylene glycol, tetramethylene glycol, neopentyl glycol, hexamethylene glycol, nonamethylene glycol, trimethylolethane, tetramethylolethane, trimethylolpropane, glycerol, pentaerythritol, dipentaerythritol, sorbitol, and their ethylene oxide adducts, propylene oxide adducts, diethanolamine, triethanolamine or the like, for example, ethylene glycol

di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, tetramethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, hexamethylene glycol di(meth)acrylate, nonamethylene glycol di(meth)acrylate, trimethylolethane tri(meth)acrylate, tetramethylolmethane tri(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane ethylene oxide adduct tri(meth)acrylate, glycerol di(meth)acrylate, glycerol tri(meth)acrylate, glycerol propylene oxide adduct tri(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol di(meth)acrylate, dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, sorbitol tri(meth)acrylate, sorbitol tetra(meth)acrylate, sorbitol penta(meth)acrylate, sorbitol hexa(meth)acrylate or the like, and their corresponding crotonate, isocrotonate, maleate, itaconate, citraconate, and the like.

Examples of an ester of an unsaturated carboxylic acid and an aromatic polyhydroxy compound such as hydroquinone, resorcin, pyrogallol or the like, include hydroquinone diacrylate, hydroquinone dimethacrylate,

resorcin diacrylate, resorcin dimethacrylate, pyrogallol triacrylate, and the like.

An ester obtained by esterification of an unsaturated carboxylic acid with a polyhydric carboxylic acid and a polyhydric hydroxy compound is not always a single material, but their typical examples include a condensate of acrylic acid, phthalic acid and ethylene glycol; a condensate of acrylic acid, maleic acid and diethylene glycol; a condensate of methacrylic acid, terephthalic acid and pentaerythritol; a condensate of acrylic acid, adipic acid, butanediol and glycerin; and the like.

Other examples of an ethylenic compound include urethane acrylates such as an adduct of tolylene diisocyanate and hydroxyethyl acrylate; epoxy acrylates such as an adduct of diepoxy compound and hydroxyethyl acrylate; acrylamides such as ethylene bisacrylamide or the like; acrylic acid esters such as diacryl phthalate or the like; a vinyl group-containing compound such as divinyl phthalate; and the like.

Examples of said urethane (meth)acrylates include an aliphatic polyisocyanate such as hexamethylene diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, lysine methyl ester diisocyanate, lysine methyl ester triisocyanate, dimer acid diisocyanate, 1,6,11-undecatriisocyanate, 1,3,6-hexamethylene triisocyanate, 1,8-diisocyanate-4-isocyanate methyloctane or the like,

an alicyclic polyisocyanate such as cyclohexane diisocyanate, dimethylcyclohexane diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), isophorone diisocyanate, bicycloheptane triisocyanate or the like, an aromatic polyisocyanate such as p-phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, xylylene diisocyanate, tetramethylxylylene diisocyanate, 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, 1,5-naphthalene diisocyanate, tris(isocyanatephenylmethane), tris(isocyanatephenyl)thiophosphate or the like, reaction products of a polyisocyanate compound such as a heterocyclic polyisocyanate including isocyanurate and a hydroxy(meth)acrylate compound such as hydroxymethyl(meth)acrylate, hydroxyethyl(meth)acrylate, glycerol di(meth)acrylate, pentaerythritol tri(meth)acrylate or tetramethylolethane tri(meth)acrylate, and the like.

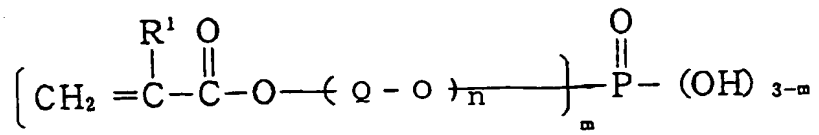
Also, examples of said epoxy(meth)acrylates include an aliphatic polyepoxy compound such as (poly)ethylene glycol polyglycidyl ether, (poly)propylene glycol polyglycidyl ether, (poly)tetramethylene glycol polyglycidyl ether, (poly)pentamethylene glycol polyglycidyl ether, (poly)neopentyl glycol polyglycidyl ether, (poly)hexamethylene glycol polyglycidyl ether, (poly)trimethylolpropane polyglycidyl ether, (poly)glycerol polyglycidyl ether, (poly)sorbitol

polyglycidyl ether or the like, a heterocyclic polyoxy compound such as sorbitan polyglycidyl ether, triglycidyl isocyanurate, triglycidyl tris(2-hydroxyethyl)isocyanurate or the like, and a reaction product of (meth)acrylic acid or hydroxy(meth)acrylate compound with a polyepoxy compound of an aromatic polyepoxy compound such as phenol novolak polyepoxy compound, bromated phenol novolak polyepoxy compound, (o-, m-, p-)cresol novolak polyepoxy compound, bisphenol A polyepoxy compound, bisphenol F polyepoxy compound or the like.

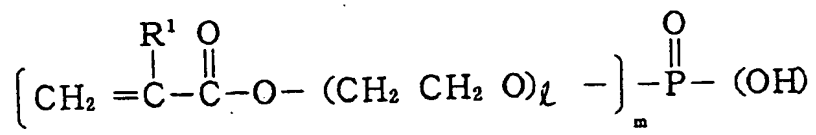
Among the above listed ethylenic compounds, it is particularly preferable to include a monomer of acrylate or methacrylate.

Further, preferable examples of an ethylenic compound include a phosphoric acid ester compound having at least one (meth)acryloyl group, and the aimed effect of the present invention can be satisfactorily achieved by using a photopolymerizable photosensitive composition containing said phosphoric ester compound in combination with an aluminum support anodized with an electrolyte containing sulfuric acid.

Said phosphoric acid ester compound containing at least one (meth)acryloyl group is not specially limited so long as it is a phosphoric acid ester having at least one (meth)acryloyl group in its structure, and their examples are expressed by the following formula (I).



(Ia)



(Ib)

(In the above formulae (Ia) and (Ib), R^1 is a hydrogen atom or a methyl group, Q is a C_{1-25} divalent alkylene chain, ℓ is an integer of from 1 to 25, n is an integer of from 1 to 2, and m is 1, 2 or 3.)

In the formula (I), n is preferably 1, and Q has preferably a carbon number of from 1 to 10, particularly 1 to 4. Their examples include (meth)acryloyloxyethyl phosphate, bis[(meth)acryloyloxyethyl]phosphate, (meth)acryloyloxyethylene glycol phosphate, and the like, and they may be used respectively alone or in a mixture. When said phosphoric acid ester compound is used, it may preferably be contained in an amount of from 1 to 50 wt%, particularly from 5 to 50 wt%, of the total ethylenic compounds. If it is contained in the above range, there is tendency that non-image parts are hardly stained.

Hereinafter, a photopolymerization initiator is explained. Any photopolymerization initiator can be used if it initiates the polymerization of said ethylenic compound. A photopolymerization initiator generally contains a radical-generating agent, a sensitizer and optionally a polymerization accelerator. The radical-

generating agent generates an active radical when a photopolymerizable composition is irradiated with active light, and initiates the polymerization of said ethylenic compound. Any radical-generating agent can be satisfactorily used if it has a photosensitivity to from ultraviolet light to visible light and further to infrared light. Among them, examples of a radical-generating agent causing an action with a photo-excited sensitizer include hexaarylbiimidazoles, a titanocene compound, a halogenated hydrocarbon derivative, a diaryliodonium salt, an organic peroxide, and the like. Among them, a system employing hexaarylbiimidazoles or a titanocene compound is preferable in respect of sensitivity, shelf life, and adhesiveness of a coating film to a substrate.

Various kinds of hexaarylbiimidazoles can be used, examples of which include 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(p-fluorophenyl)biimidazole, 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetra(p-iodophenyl)biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(p-chloronaphthyl)biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(p-chlorophenyl)biimidazole, 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetra(p-chloro-p-ethoxyphenyl)biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(o,p-dichlorophenyl)biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(o,p-dibromophenyl)biimidazole, 2,2'-bis(o-bromophenyl)-

4,4',5,5'-tetra(o,p-dichlorophenyl)biimidazole, 2,2'-bis(o,p-dichlorophenyl)-4,4',5,5'-tetra(o,p-dichlorophenyl)biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(p-chloronaphthyl)biimidazole, and the like. These imidazoles may be used optionally in combination with other kinds of biimidazoles. Biimidazoles can be easily prepared, for example, by a method disclosed in Bull. Chem. Soc. Japan, 33,565(1960) and J. Org. Chem. 36[16]2262(1971).

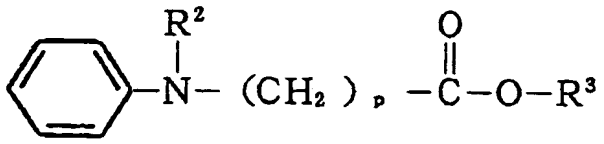
Various kinds of titanocene compounds can be used, but may be optionally selected from various titanocene compounds disclosed in JP-A-59-152396 and JP-A-61-151197. Examples of the titanocene compounds include dicyclopentadienyl-Ti-dichloride, dicyclopentadienyl-Ti-bisphenyl, dicyclopentadienyl-Ti-bis-2,3,4,5,6-pentafluorophenyl, dicyclopentadienyl-Ti-bis-2,3,5,6-tetrafluorophenyl, dicyclopentadienyl-Ti-bis-2,4,6-trifluorophenyl, dicyclopentadienyl-Ti-bis-2,6-difluorophenyl, dicyclopentadienyl-Ti-bis-2,4-difluorophenyl, dimethylcyclopentadienyl-Ti-bis-2,3,4,5,6-tetrafluorophenyl, dimethylcyclopentadienyl-Ti-bis-2,6-difluorophenyl, dicyclopentadienyl-Ti-bis-2,6-difluoro-3-(1-pyrrolyl)phenyl, and the like.

Hereinafter, a sensitizer in the photopolymerization initiator is explained. The sensitizer in the present invention means a compound effectively generating an active radical in the presence of said radical-generating

agent by activating the radical-generating agent by irradiation with ultraviolet light, visible light or infrared light.

Typical examples of the sensitizer effectively generating an active radical by irradiation with visible light include a photo-reducible dye such as erythron or eosine Y, a triphenylmethane type leuco dye such as leuco crystal violet or leuco-malachite green as disclosed in U.S. Patent No. 3,479,185, aminophenylketones such as Michler's ketone or aminostyryl ketone as disclosed in U.S. Patent No. 3,549,367 and U.S. Patent No. 3,652,275, β-diketones as disclosed in U.S. Patent No. 3,844,790, indanones as disclosed in U.S. Patent No. 4,162,162, cumalin type dyes as disclosed in JP-A-6-301208, JP-A-8-129258, JP-A-8-129259, JP-A-8-146605 and JP-A-8-211605, ketocumalins as disclosed in JP-A-52-112681, aminostyrene derivatives or aminophenylbutadiene derivatives as disclosed in JP-A-59-56403, aminophenyl heterocyclic compounds as disclosed in U.S. Patent No. 4,594,310, durolidine heterocyclic compounds as disclosed in U.S. Patent No. 4,966,830, pyrromethene type dyes as disclosed in JP-A-5-241338, JP-A-7-5685 and JP-A-10-144242, and the like. Among them, when exposed to a laser light of 450 to 600 nm, cumalin type or pyrromethine type dyes are preferable, and when exposed to a laser light of 390 to 430 nm, dialkylaminobenzene type compounds are preferable, in respect of sensitivity.

Further, a photopolymerization-initiating performance can be raised optionally by adding a polymerization accelerator to a photopolymerization initiator, and examples of the polymerization accelerator include a mercapto group-containing compound such as 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 3-mercapt-1,2,4-triazole or the like, a N-aryl-α-amino acid or its derivatives such as N-phenylglycine, N,N-dialkylbenzoic acid alkyl ester, N,N-dialkylaminobenzoic acid ester, N-phenylglycine, or its ammonium or sodium salt, or its ester derivatives, N-phenylalanine, or its ammonium or sodium salt, or its ester derivatives, and a hydrogen-donating compound such as a compound expressed by the following formula (II).



(II)

[In the formula (II), R^2 is a hydrogen atom or an alkyl group which may have a substituent, R^3 is a hydrogen, an alkyl group which may have a substituent, a vinyl group which may have a substituent, an allyl group which may have a substituent, a (meth)acryloyloxy group which may have a substituent, an aryl group which may have a substituent or an aromatic heterocyclic group which may have a substituent, and the benzene ring may have a substituent, and p is an integer of from 2 to 10.]

Examples of a substituent on the benzene ring

include an alkyl group which may have a substituent, an alkoxy group which may have a substituent, an acyl group which may have a substituent, an alkoxycarbonyl group which may have a substituent, a vinyl group which may have a substituent, an allyl group which may have a substituent, a (meth)acryloyloxy group which may have a substituent, an aryl group which may have a substituent or an aromatic heterocyclic group which may have a substituent. Among them, particularly preferable examples include a compound having a mercapto group such as 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 3-mercapto-1,2,4-triazole and the like.

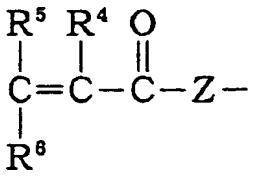
Hereinafter, a high molecular binder is explained.

The high molecular binder is a component imparting a film-forming performance or a viscosity-controlling performance, examples of which include an alkali-soluble high molecular binder, and among them a high molecular binder having a carboxyl group in a molecule is preferable in respect of alkali-developing property.

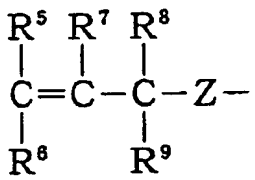
Examples of the high molecular binder having a carboxyl group in a molecule include a homopolymer or copolymer of (meth)acrylic acid, (meth)acrylic acid ester, (meth)acrylamide, maleic acid, (meth)acrylonitrile, styrene, vinyl acetate, vinylidene chloride, maleimide or the like, and polyethylene oxide, polyvinyl pyrrolidone, polyamide, polyurethane, polyester, polyether,

polyethylene terephthalate, acetylcellulose, polyvinylbutyral, and the like. Among them, a preferable example includes a copolymer containing at least one kind of (meth)acrylic acid ester and (meth)acrylic acid as copolymerizable components. The high molecular binder having a carboxyl group in a molecule preferably has an acid value of from 10 to 250 and a weight average molecular weight (hereinafter referred to as "Mw") of from 5,000 to 500,000.

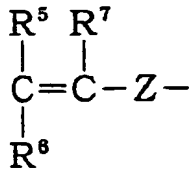
These high molecular binders preferably have an unsaturated bond on a side chain, particularly at least one unsaturated bond expressed by the following formula (II)



(IIIa)



(IIIb)



(IIIc)

(In the above formulae, R^4 is a hydrogen atom or a methyl group, and each of R^5 to R^8 is independently a hydrogen atom, a halogen atom, an amino group, a dialkylamino group, a carboxyl group, an alkoxycarbonyl group, a sulfo group, a nitro group, a cyano group, an alkyl group which

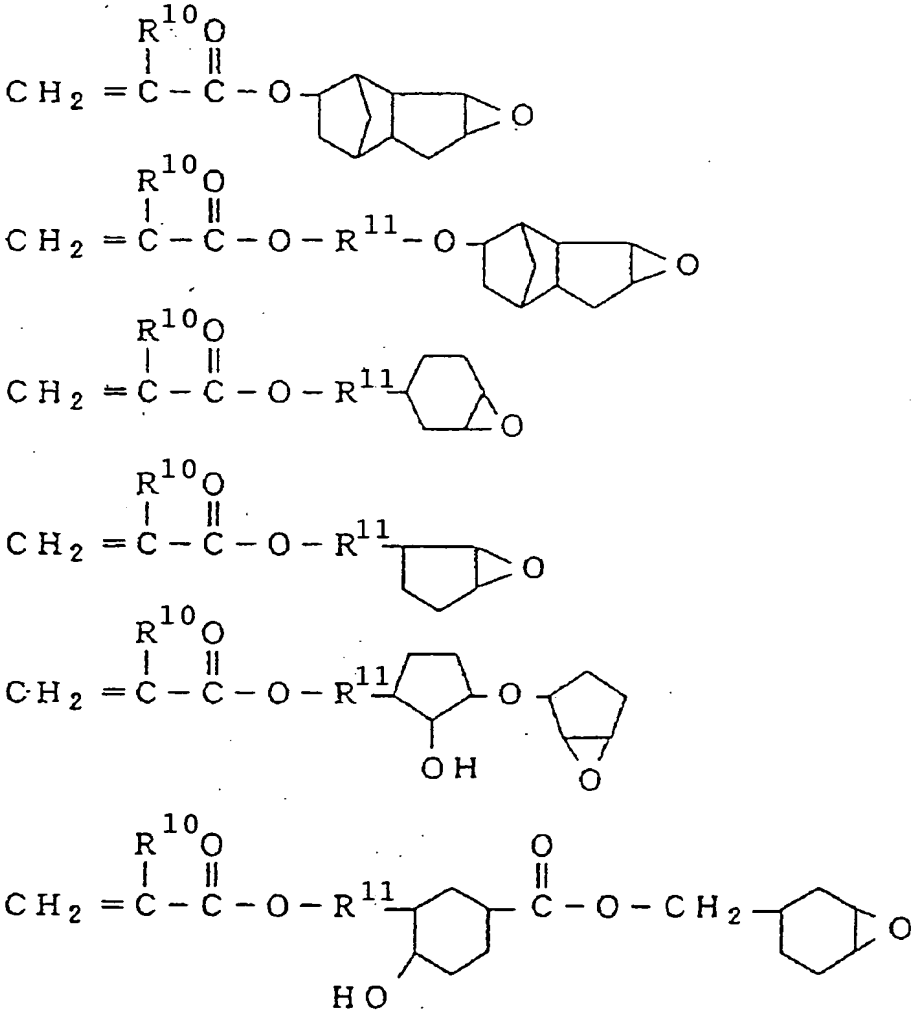
may have a substituent, an aryl group which may have a substituent, an alkoxy group which may have a substituent, an aryloxy group which may have a substituent, an alkylamino group which may have a substituent, an arylamino group which may have a substituent, an alkylsulfonyl group which may have a substituent or an arylsulfonyl group which may have a substituent, and Z is an oxygen atom, a sulfur atom, an imino group or an alkylimino group.)

Examples of a substituent which may be bonded to the above alkyl group are not specially limited so long as it does not remarkably lower the reactivity of a carbon-carbon double bond, but are usually selected from a halogen atom, an alkyl group, a phenyl group, a cyano group, a nitro group, an alkoxy group, an alkylthio group, a dialkylamino group, and the like.

Among them, R^4 is preferably a hydrogen atom or a methyl group, and each of R^5 and R^6 is preferably independently a hydrogen atom, a lower alkyl group, an alkoxy group, a dialkylamino group or a cyano group.

Examples of a high molecular binder having an unsaturated bond on a side chain and containing a carboxyl group in a molecule include a compound obtained by reacting a part of carboxyl groups of a high molecular binder having a carboxyl group in a molecule with an epoxy group-containing unsaturated compound as disclosed in JP-A-9-346144.

Examples of the epoxy group-containing unsaturated compound include an aliphatic epoxy group-containing unsaturated compound such as glycidyl(meth)acrylate, allylglycidyl ether, α-ethylglycidyl acrylate, crotonylglycidyl ether, glycidyl crotonate, glycidyl isocrotonate, itaconic acid monoalkyl ester monoglycidyl ester, fumaric acid monoalkyl ester monoglycidyl ester, maleic acid monoalkyl ester monoglycidyl ester or the like, and cycloaliphatic epoxy group-containing unsaturated compounds expressed by the following structures.



(In the above formulae, R^{10} is a hydrogen atom or a methyl group, and R^{11} is a C_{1-6} divalent aliphatic saturated hydrocarbon group.)

A high molecular binder having an ethylenic unsaturated bond on a side chain as expressed by the above formula (IIIa) is obtained by reacting a carboxyl group-containing polymer with a cycloaliphatic epoxy group-containing unsaturated compound or the like at a temperature of from 80 to 120°C for 1 to 50 hours in such a manner as to react from 5 to 90 mol%, preferably from 30 to 70 mol% of the carboxyl group contained in the carboxyl group-containing polymer.

Also, a high molecular binder having an ethylenic unsaturated bond on a side chain as expressed by the formula (IIIb) can be obtained by copolymerizing a compound having at least two unsaturated groups such as allyl(meth)acrylate, 3-allyloxy-2-hydroxypropyl(meth)acrylate, cinnamyl(meth)acrylate, crotonyl(meth)acrylate, methallyl(meth)acrylate, N,N-diallyl(meth)acrylamide or the like with an unsaturated carboxylic acid such as (meth)acrylic acid or unsaturated carboxylic acid ester in such a manner as to make the content of the former compound having at least two unsaturated groups from 10 to 90 mol%, preferably from 30 to 80 mol%, in the total copolymer, and a high molecular binder having an ethylenic unsaturated bond as expressed by the above formula (IIIc) can be obtained by

copolymerizing a compound having at least two unsaturated groups such as vinyl(meth)acrylate, 1-chlorovinyl(meth)acrylate, 2-phenylvinyl(meth)acrylate, 1-propenyl(meth)acrylate, vinyl crotonate, vinyl(meth)acrylamide or the like with an unsaturated carboxylic acid such as (meth)acrylic acid or unsaturated carboxylic acid ester in such a manner as to make the content of the former compound having at least two unsaturated groups from 10 to 90 mol%, preferably from 30 to 80 mol%, in the total copolymer.

Hereinbefore, main components of a photopolymerizable composition for forming a photosensitive layer are explained in details. A photopolymerization initiator used preferably contains a sensitizer preferably in an amount of from 0.01 to 20 parts by weight, more preferably from 0.05 to 10 parts by weight, an activator preferably in an amount of from 0.1 to 80 parts by weight, more preferably from 0.5 to 50 parts by weight, and a polymerization accelerator preferably in an amount of from 0.1 to 80 parts by weight, more preferably from 0.05 to 60 parts by weight, to 100 parts by weight of an ethylenic compound, and a high molecular binder is used preferably in an amount of from 10 to 400 parts by weight, more preferably from 20 to 200 parts by weight.

Also, in addition to the above component, the photopolymerizable composition may further contain other

materials depending on its use. For example, the photopolymerizable composition may further contain a thermal polymerization inhibitor such as hydroquinone, p-methoxyphenol, 2,6-di-t-butyl-p-cresol or the like; a colorant comprising an organic or inorganic dye or pigment; a plasticizer such as dioctyl phthalate, didodecyl phthalate, tricresyl phosphate or the like, a sensitivity improver such as tertiary amine or thiol, a coating property improver such as a surfactant including a fluorine type surfactant, a development-accelerating agent, and other additives such as a dye precursor, or the like.

A preferable amount of each of the above-mentioned various additives is generally at most 2 parts by weight of a thermal polymerization inhibitor, at most 20 parts by weight of a colorant, at most 40 parts by weight of a plasticizer, at most 10 parts by weight of a coating property improver or a development accelerator, and at most 30 parts by weight of a dye precursor, to 100 parts by weight of an ethylenic compound.

The above-mentioned photopolymerizable composition is diluted with an appropriate solvent, and is coated on the above support and is dried to form a photosensitive layer.

Examples of the solvent used for coating the photopolymerizable composition solution are not specially limited, provided that it has a satisfactory solubility

to components used and provides a satisfactory coating property, examples of which include a cellosolve type solvent such as methyl cellosolve, ethyl cellosolve, methyl cellosolve acetate, ethyl cellosolve acetate or the like, a propylene glycol type solvent such as propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monobutyl ether acetate, dipropylene glycol dimethyl ether or the like, an ester type solvent such as butyl acetate, amyl acetate, ethyl butyrate, butyl butyrate, diethyl oxalate, ethyl pyruvate, ethyl-2-hydroxy butyrate, ethyl acetoacetate, methyl lactate, ethyl lactate, methyl 3-methoxypropionate or the like, an alcohol type solvent such as heptanol, hexanol, diacetone alcohol, furfuryl alcohol or the like, a ketone type solvent such as cyclohexanone, methylamyl ketone or the like, a high polar solvent such as dimethylformamide, dimethylacetamide, N-methylpyrrolidone or the like, or their mixture solvents, or further mixtures mixed with an aromatic hydrocarbon. The solvent is used generally in a weight amount of from 1 to 20 times to the total amount of the photopolymerizable composition.

The composition can be coated in a well known method such as dip coating, rod coating, spinner coating, spray coating, roll coating or the like. A coating film

thickness is usually from 0.1 to 10 g/m^2, preferably from 0.5 to 5 g/m^2, but in the first feature of the present invention, a dry film thickness must be from 1.2 to 4 g/m^2, and if the dry film thickness is thinner than this range, storage properties become poor (a sensitivity lowers and a non-image part is not satisfactorily developed at the time of development), and if the dry film thickness is thicker than this range, a sensitivity is insufficient, and the effect of the first feature of the present invention is not fully achieved. The dry film thickness is preferably from 1.2 to 3.5 g/m^2. The film thickness of the photosensitive layer of the first feature of the present invention is equivalent to a preferable film thickness of the photosensitive layer of the second feature of the present invention. A drying temperature is preferably from 30 to 150°C, more preferably from 40 to 110°C.

In the photosensitive lithographic printing plate of the present invention, a protective layer is provided as an oxygen-shielding layer for inhibiting polymerization by oxygen on a photopolymerizable photosensitive layer as an upper layer. The protective layer usually contains a water-soluble high molecular binder, and well known various water-soluble high molecular compounds are illustrated, examples of which include polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxide, cellulose, a partially acetal-modified product of polyvinyl alcohol,

its cation-modified product by a quaternary ammonium salt or the like, its anion-modified derivative by sodium sulfonate or the like, methyl cellulose, carboxymethyl cellulose, hydroxylethyl cellulose, hydroxypropyl cellulose, gelatin, gum arabic, methyl vinyl ether-maleic anhydride copolymer, a partially saponified product of polyacrylic acid ester, vinylpyrrolidone, a carboxyl group-containing compound such as an unsaturated carboxylic acid including (meth)acrylic acid, itaconic acid or the like and its derivatives, a copolymer comprising a hydroxy group-containing compound including hydroxyethyl(meth)acrylamide or the like as a copolymerizable component, and the like. The water-soluble high molecular compound has a weight average molecular weight of from 1,000 to 300,000, preferably from 4,000 to 100,000. Among them, polyvinyl alcohol or its derivative having a high oxygen gas barrier property is particularly preferable. Also, its saponification degree is preferably from 70 to 99 mol%, more preferably from 85 to 95 mol%.

Further, in view of adhesiveness to a photosensitive layer, it is preferable to include a vinylpyrrolidone type polymer such as polyvinyl pyrrolidone, vinylpyrrolidone-vinyl acetate copolymer or the like, an acrylic polymer emulsion, a diisocyanate compound, p-toluenesulfonic acid, hydroxyacetic acid or the like, and it is preferable to contain these materials in an amount

of from 0.1 to 60 parts by weight, more preferably from 1 to 50 parts by weight, to 100 parts by weight of said polyvinyl alcohol and its derivatives.

These water-soluble high molecular compounds are used respectively alone or in a mixture, and preferably contain an organic acid such as succinic acid or an organic acid salt such as ethylenediamine tetraacetic acid in view of storage property, and in order to improve a coating property, they may further contain a nonionic surfactant such as polyoxyethylene alkylphenyl ether, an anionic surfactant such as sodium dodecylbenzene sulfonate and a cationic surfactant such as alkyltrimethylammonium chloride, and a defoaming agent, a dye, a plasticizer, a pH-adjustor or the like in an amount of at most 10 parts by weight to 100 parts by weight of said polyvinyl alcohol and its derivative. A coating process of the protective layer may be carried out by a well known method in the same manner as in the coating of a photosensitive layer. A coating film thickness is usually from 1 to 10 g/m^2, preferably from 1.5 to 7 g/m^2, but in the first feature of the present invention, a dry film thickness must be from 2 to 7 g/m^2. If the dry film thickness is thinner than this range, a sensitivity is insufficient, and on the other hand, if the dry film thickness is thicker than this range, a storage property becomes poor, and consequently a sensitivity is lowered and a non-image part is not

satisfactorily developed. Thus, the effect of the present invention is not fully achieved. A drying temperature is usually from 30 to 110°C, preferably from 40 to 70°C. The protective layer film thickness of the first feature of the present invention is equivalent to a preferable protective film thickness of the second feature of the present invention.

The method for treating a photosensitive lithographic printing plate in accordance with the present invention comprises exposing the photosensitive lithographic printing plate to laser light, developing, and then carrying out post-exposure.

Examples of the laser exposure light source includes well known laser light sources such as helium cadmium laser, argon ion laser, FD-YAG laser, helium neon laser, semiconductor layer, YAG laser, ruby laser or the like, and more particular preferable examples include a semiconductor laser of blue-violet zone of from 390 to 430 nm, an argon ion laser of in the vicinity of 488 nm wavelength, a FD-YAG laser of in the vicinity of 532 nm wavelength, a YAG laser or a semiconductor laser of from 700 to 1,300 nm, or the like.

An appropriate value of the laser exposure amount varies depending on a laser light source or a type of plotter used, but preferably from 0.5 to 100 $\mu J/cm^2$ in the semiconductor laser of blue-violet zone of from 390 to 430 nm, from 5 to 500 $\mu J/cm^2$ in the FD-YAG laser of in

the vicinity of 532 nm and the argon ion laser of in the vicinity of 488 nm, and from 0.5 to 200 mJ/cm^2 in the semiconductor laser of from 700 to 1,300 nm.

If necessary, after laser exposure, the exposed printing plate may be subjected to heat treatment at a temperature in the range of from 40 to 300°C, but may be developed with a developer without heat treatment.

In the treating method of the present invention, after subjecting the photosensitive lithographic printing plate to image-exposure by laser light, the protective layer may be washed with water before development to remove all or most part of the protective layer. The method of washing with water is not particularly limited, but examples include a method of dipping into water to dissolve, a method of dissolving by applying shower-like water thereto, and a method of removing with a brush in the state of dipped in water or sprayed with water. The washing with water is carried out generally at a temperature of from 4 to 70°C, preferably from 10 to 50°C, more preferably from 15 to 30°C, and washing time varies depending on a method for washing, but is usually from 1 second to 5 minutes. Washing water may optionally contain a surfactant, a water-miscible organic solvent or the like.

The developer used in the present invention is an aqueous solution containing an alkali metal silicate. Examples of the alkali metal silicate include potassium

silicate, sodium silicate, lithium silicate, potassium metasilicate, sodium metasilicate and the like, and its concentration is from 0.1 to 10 wt%. Also, in addition to the alkali metal silicate, an inorganic alkali agent such as potassium hydroxide, sodium hydroxide, lithium hydroxide, sodium tertiary phosphate, sodium secondary phosphate, sodium carbonate, potassium carbonate, sodium bicarbonate or the like, and an organic amine compound such as trimethylamine, diethylamine, isopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine or the like may be used as an alkali agent in combination therewith.

The developer of the present invention preferably further contains a surfactant to improve an image quality and to reduce a developing time. Examples of the surfactant used in the developer of the present invention include a nonionic surfactant such as polyoxyethylene alkyl ethers including polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether or the like, polyoxyethylene alkylallyl ethers including polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether or the like, polyoxyethylene alkyl esters including polyoxyethylene stearate or the like, sorbitan alkyl esters including sorbitan monolaurate, sorbitan monostearate, sorbitan distearate, sorbitan monooleate, sorbitan sesquioleate, sorbitan trioleate or the like, monoglyceride alkyl

esters including glycerol monostearate, glycerol monooleate or the like, and the like; an anionic surfactant such as alkylbenzene sulfonates including sodium dodecylbenzene sulfonate or the like, alkylnaphthalene sulfonates including sodium butylnaphthalene sulfonate, sodium pentylnaphthalene sulfonate, sodium hexylnaphthalene sulfonate, sodium octylnaphthalene sulfonate or the like, alkylsulfates including sodium laurylsulfate or the like, alkylsulfonates including sodium dodecylsulfonate or the like, sulfosuccinic acid ester salts including sodium dilaurylsulfosuccinate, and the like; and an amphoteric surfactant such as alkylbetaines including laurylbetaine, stearylbetaine or the like, amino acids or the like. Particularly preferable examples include an anionic surfactant such as alkylnaphthalene sulfonates.

These surfactants may be used alone or in combination thereof. Also, the content of these surfactants in the developer is preferably from 0.1 to 5 wt% in terms of effective components.

The developer used in the present invention includes not only a virgin developer used at the initial stage of development but also a refreshed developer (i.e. "running developer") retaining an activity obtained by supplying a supplying developer to a used developer, the developing performance of which was lowered by treating a photosensitive lithographic printing plate.

Also, the developer used in the present invention includes any developer practically capable of treating a photosensitive lithographic printing plate.

The developer used in the present invention may further contain the following additional components in addition to the above components. Examples of the additional components include an organic carboxylic acid such as benzoic acid, phthalic acid, p-ethylbenzoic acid, p-n-propylbenzoic acid, p-isopropylbenzoic acid, p-n-butylbenzoic acid, p-t-butylbenzoic acid, p-t-butylbenzoic acid, p-2-hydroxyethylbenzoic acid, decanoic acid, salicylic acid, 3-hydroxy-2-naphthoic acid or the like; an organic solvent such as isopropyl alcohol, benzyl alcohol, ethyl cellosolve, butyl cellosolve, phenyl cellosolve, propylene glycol, diacetone alcohol or the like; and a chelating agent, a reducing agent, a dye, a pigment, a water softener, an antiseptic agent, and the like. The developer preferably has a pH value of from 9 to 14, more preferably from 9 to 12.

The development can be carried out by a well known developing method such as dipping development, spraying development, brush development, ultrasonic wave development or the like, preferably at a temperature of from 10 to 60°C, more preferably from 15 to 45°C, for 5 seconds to 10 minutes. An oxygen-shielding layer may be previously removed with water, or may be removed at the time of development.

The treating method of the present invention is characterized by carrying out post-exposure (whole surface exposure) to an image obtained by this development, and examples of a light source used for the post-exposure are not specially limited but include a carbon arc, a high pressure mercury lamp, a xenon lamp, a metal halide lamp, a fluorescent lamp, a tungsten lamp, a halogen lamp or the like, which has a wavelength of from 200 to 1,100 nm. Light emitted from these light sources may be used by controlling wavelength through a filter or the like. Among them, it is preferable to use a mercury lamp in view of printing resistance of a printing plate.

As a mercury lamp, any of an ultra high pressure mercury lamp, a high pressure mercury lamp and a low pressure mercury lamp can be used, and as a lighting system, any of a stationary lighting system, a flash lighting system and an instant lighting system may be used.

A light amount of post-exposure is not specially limited, but a higher effect can be expected if the light amount is larger, and the light amount is usually in the range of from 10 to 10,000 mJ/cm^2, preferably in the range of from 10 to 1,000 mJ/cm^2 in view of rationalization of a step of preparing a printing plate. As a method for exposure, the exposure may be carried out by stopping an image or by continuously moving an image.

In the treating method of the second feature of the

present invention, it is necessary for carrying out post-light exposure after the development to make a light intensity at least 20 mW/cm^2 on the surface to be exposed (an image-forming surface). Particularly, the light intensity is preferably at least 30 mW/cm^2, more preferably at least 50 mW/cm^2, most preferably at least 70 mW/cm^2. If the light intensity is lower than the above-mentioned range, it is difficult to obtain a sufficient image strength. It is better if the light intensity is higher, and its upper limit is not specially limited, but if it is too excessively high, an image strength-improving effect is saturated and it is not favorable from an economical viewpoint. Thus, the upper limit of the light intensity is usually 700 mW/cm^2, preferably 500 mW/cm^2, more preferably 300 mW/cm^2.

As a light source for post-light exposure, the same light sources as mentioned above can be used. Also, as a method for light exposure, light exposure may be carried out by stopping an image or by continuously moving an image, and its light exposure amount is preferably in the range of from 10 to 10,000 mJ/cm^2, more preferably from 50 to 8,000 mJ/cm^2.

In these light exposure methods, in order to make a light intensity on the surface to be exposed at least 20 mW/cm^2, a light exposure method by raising an output (W) of a light source which includes a method of making an output of a light source used larger or making an output

per unit length larger in the case of a bar-like light source or a light exposure method by making an image-forming surface closer to a light source, may be employed. As a light source for achieving such a light intensity, the above-mentioned light sources for post-light exposure may be used, and when a mercury lamp is used among them, a satisfactory image strength can be obtained without specially employing a step for heating a printing plate. Thus, a mercury lamp is particularly preferable. The shape of a mercury lamp is not limited, but preferable examples include a bar-like type mercury lamp (H03-L31, H04-L41 or the like manufactured by EYEGRAPHICS CO.), a self ballast mercury lamp (BHF200/220 V 300 W manufactured by EYEGRAPHICS CO.), a sphere-like type mercury lamp used for carrying out post-light exposure of a usual photosensitive lithographic printing plate, and the like.

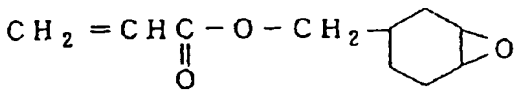
In the second feature of the present invention, a temperature of a surface to be exposed at the post-exposure is preferably from 40 to 300°C, more preferably from 50 to 200°C. In order to make the temperature of the surface to be treated in the above-mentioned range, a method for raising an output of a light source for light exposure, a method for light exposure by placing a light source closer to the surface to be exposed, or a method for heating by a hot plate, a dryer or a ceramic heater, may be employed.

EXAMPLES

Hereinafter, the present invention is more concretely explained by referring to the following Examples, but should not be limited thereto.

Preparation of high molecular binder-1

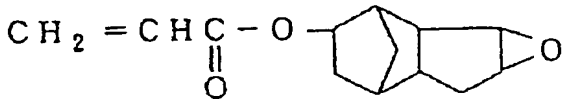
200 Parts by weight of a copolymer of methyl methacrylate/isobutyl methacrylate/isobutyl acrylate/methacrylic acid=35/20/10/35 mol% (charge ratio) having a weight average molecular weight (Mw) of 70,000 (hereinafter referred to as "base resin-1"), 75 parts by weight of an unsaturated compound having the following cycloaliphatic epoxy group, 2.5 parts by weight of p-methoxyphenol, 8 parts by weight of tetrabutylammonium chloride, and 800 parts by weight of propylene glycol monomethyl ether acetate were placed in a reactor, and were reacted at 110°C for 24 hours in air with stirring to obtain a solution of high molecular binder-1 (acid value=60, an unsaturated group was reacted with 60% of the total methacrylic acid component of base resin-1).



Preparation of high molecular binder-2

855 Parts by weight of a copolymer of α-methylstyrene/acrylic acid (tradename "SCX-690" manufactured by Johnson Co., acid value=240, Mw=15,000), 490 parts by weight of an unsaturated compound containing

the following cycloaliphatic epoxy group, 1.3 parts by weight of p-methoxyphenol, 4.3 parts by weight of tetraethylammonium chloride, and 1,800 parts by weight of propylene glycol monomethyl ether acetate were placed in a reactor, and were reacted at 120°C for 15 hours in air with stirring to obtain a solution of high molecular binder-2 (acid value=about 170, an unsaturated group was reacted with about 50% of the total methacrylic acid component of SCX-690).



Support-1

An aluminum plate was degreased with 3% sodium hydroxide, and was then subjected to etching in a nitric acid bath of 18.0 g/l at 25°C and a current density of 80 A/dm^2 for 15 seconds, and was then subjected to desmut treatment with a 1% sodium hydroxide aqueous solution at 50°C for 5 seconds, and was then neutralized with a 10% nitric acid aqueous solution at 25°C for 5 seconds. After washing with water, the aluminum plate thus obtained was anodized in a 30% sulfuric acid bath under conditions of 30°C and 10 A/dm^2 for 16 seconds, and was washed with water and dried to obtain support-1 having a Ra value of 0.55 μm.

Support-2

An aluminum plate was degreased with 3% sodium

hydroxide, and was then subjected to etching in a hydrochloric acid bath of 11.5 g/l at 25°C and a current density of 80 A/dm^2 for 11 seconds, and was then subjected to desmut treatment with a 1% sodium hydroxide aqueous solution at 50°C for 5 seconds, and was then neutralized with a 10% nitric acid aqueous solution at 25°C for 5 seconds. After washing with water, the aluminum plate was anodized in a 30% sulfuric acid bath under conditions of 30°C and 10 A/dm^2 for 16 seconds, and was washed with water and dried to obtain support-2 having a Ra value of 0.63 μm.

Support-3 (comparative support)

Support-3 having a Ra value of 0.3 μm was obtained in the same manner as in the preparation of support-1, except that the etching conditions in the nitric acid bath were changed to an electric current density of 40 A/dm^2 and an etching time of 5 seconds.

Preparation of photosensitive lithographic printing plates 1 to 9

A coating solution of the following photopolymerizable composition was coated on each of the above supports-1, 2 and 3 by a bar coater, and was dried. Further, a polyvinyl alcohol aqueous solution was coated thereon and was dried to form a protective layer, thus preparing photosensitive lithographic printing plates 1 to 9. A dry film thickness of each of the photosensitive lithographic printing plates thus prepared is shown in

the following Table 1.

Coating solution of photopolymerizable composition

Ethylenic monomer shown in Table 1

Total 55 parts by weight

High molecular binder shown in Table 1

45 parts by weight

Compound of the following structure (A)

2.0 parts by weight

Titanocene compound of the following structure (B)

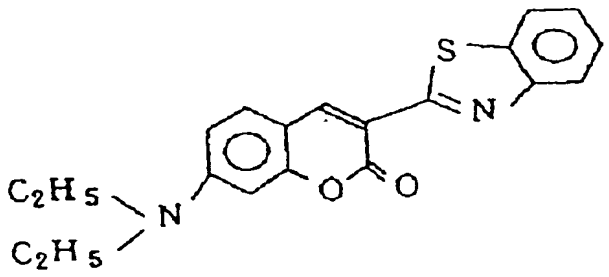
10 parts by weight

2-Mercaptobenzothiazole 5.0 parts by weight

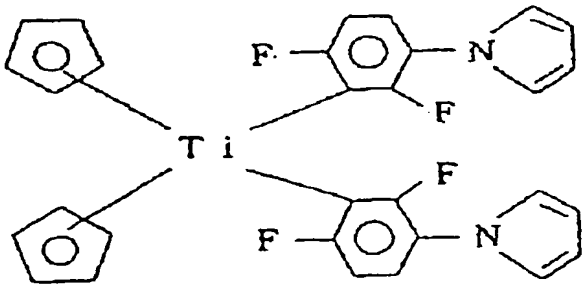
Ethyl N,N-dimethylbenzoate ester 10 parts by weight

Copper phthalocyanine pigment 3.0 parts by weight

Cyclohexanone 1090 parts by weight



(A)



(B)

Table 1

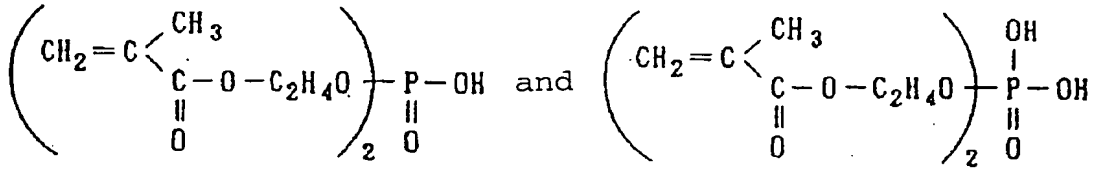
Table 1

		Photosensitive lithographic printing plate								
		1	2	3	4	5	6	7	8	9
Ethylenic monomer (part by weight)	1	5	5	5	5	5	5	10	10	10
	2	25	25	25	25	25	25	23	23	23
	3	25	25	25	25	25	25	23	23	23
High molecular binder (part by weight)	1	40	40	40	40	40	40	34	34	34
	2	5	5	5	5	5	5	10	10	10
Support		1	1	1	2	3	3	1	1	1
Thickness of photosensitive layer (g/m^2)		2	1	2	2	2	1	2	5	2
Thickness of protective layer (g/m^2)		3	3	8	3	3	3	4	4	1

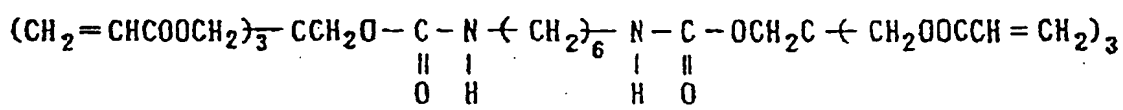
Ethylenic monomers shown in the above Table 1 are illustrated below.

1: PM-2 manufactured by Nihon Kayaku K.K.

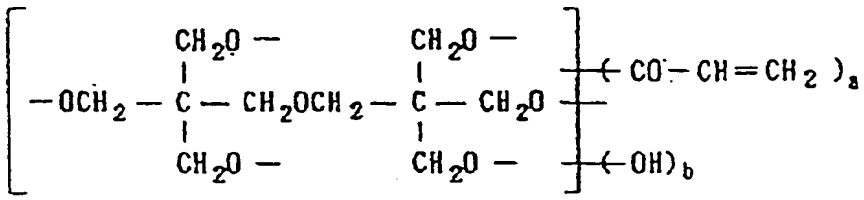
1:1 (mol ratio) mixture of



2: UA-306H manufactured by Shin Nakamura Kagaku K.K.



3: DPHA manufactured by Nihon Kayaku K.K.



a=6, b=0 and a=5, b=1

Examples 1 to 3 and Comparative Examples 1 to 12

The above prepared photosensitive lithographic printing plates 1 to 9 were subjected to internal drum system scanning light exposure with argon laser (light amount: 130 μJ/cm^2, wavelength: 488 nm).

The photosensitive lithographic printing plate 1 to 9 thus subjected to light exposure treatment as mentioned above were developed with the developers shown in the following Table 2 by using an automatic developing machine HL-860X (manufactured by Mitsubishi Chemical Corporation). A developer temperature was 30°C and a conveying speed was 60 cm/min.

Thereafter, a part of the above obtained printing plates were subjected to post-light exposure treatment with a mercury lamp (150 mJ/cm^2) in accordance with the conditions as shown in the following Table 2.

The printing plates thus obtained were subjected to printing resistance test by a printing machine (Roland RP-1). The printing resistance was evaluated by reproducibility of 2% small dots of an image part after

printing 100,000 sheets (evaluation mark ○ means that at least 80% was reproduced, and evaluation mark × means that the reproducibility was less than 80%).

Further, the above prepared photosensitive lithographic printing plates 1 to 9 were stored for 6 months, and were subjected to printing resistance test. In this test, a staining property was evaluated by a number of printing times required to reach such a normal state as not to stain a printing plate after compulsorily damping the whole surface of a printing plate with water and recharging a damping water (evaluation mark ○ means that the number of printing timés required to reach the normal state is less than 20 sheets, and evaluation mark × means that the number of printing times required to reach the normal state is at least 20 sheets).

The developers used were as follows:

Developer-1 (pH=10.8)

Potassium silicate (JIS A potassium silicate)	3 wt%
Perex NBL (manufactured by Kao K.K.) (Sodium alkylnaphthalene sulfonate: content=35%)	5 wt%
Water	92 wt%

Developer-2 (pH=11.0)

Sodium carbonate	0.5 wt%
Perex NBL (manufactured by Kao K.K.) (Sodium alkylnaphthalene sulfonate: content=35%)	5 wt%
Water	94.2 wt%

Table 2

Table 2

	Lithographic printing plate (remark)	Developer	Post-exposure	Printing resistance	Printing resistance after 6 months	Stain property (remark)
Example 1	1	1	done	○	○	○
Comparative Example 1	1	1	nil	×	×	○
Comparative Example 2	1	2 (Si absent)	done	○	○	×
Comparative Example 3	2 (Thin film photosensitive layer)	1	done	○	×	× (Developing property became poor.)
Comparative Example 4	2 (Thin film photosensitive layer)	1	nil	×	×	× (Developing property became poor.)
Comparative Example 5	3 (Thick film protective layer)	1	done	○	×	× (Developing property became poor.)
Example 2	4	1	done	○	○	○
Comparative Example 6	4	1	nil	×	×	○
Comparative Example 7	4	2 (Si absent)	done	○	○	×

Comparative Example 8	5 (Ra small)	1	done	×	×	○
Comparative Example 9	6 (Ra small)	1	done	×	×	○
Example 3	7	1	done	○	○	○
Comparative Example 10	7	1	nil	×	×	○
Comparative Example 11	8 (Thick film photosensitive layer)	1	done	×	×	○
Comparative Example 12	9 (Thin film photosensitive layer)	1	done	×	×	○

As evident from Comparative Examples 1, 6 and 10, printing resistance is poor when post-light exposure is not carried out even if the photosensitive lithographic printing plates of the present invention are employed.

As evident from Comparative Examples 2 and 7, stain property is poor when the developer used does not contain an alkali metal silicate.

As evident from Comparative Examples 3, 4 and 11, when a photosensitive layer film thickness is too thin, stain property and printing resistance after storing are poor, and when a photosensitive layer is too thick, printing resistance is poor.

As evident from Comparative Examples 5 and 12, when a protective layer film thickness is too thick, developing property and printing resistance after storing are poor, and when a protective layer is too thin, printing resistance is poor.

As evident from Comparative Examples 8 and 9, when a roughness value Ra is too small, printing resistance is poor.

On the other hand, as proved by Examples 1 to 3, the present invention provides satisfactory results in respect of all of printing resistance and stain property.

EXAMPLES 4 to 7 and COMPARATIVE EXAMPLES 13 to 15

A coating solution of a photopolymerizable composition comprising an ethylenic unsaturated compound of the following component (A), a photosensitizer, a

polymerization accelerator and a radical generator as a polymerization initiator of the following component (B), a high molecular binder of the following component (C), and other components and solvents was coated on the surface of the following aluminum plate support by a bar coater so as to obtain a dry film thickness of 2.0 g/m^2, and was dried to form a photosensitive layer of the photopolymerizable composition, and a mixture aqueous solution of polyvinyl alcohol and polyvinylpyrrolidone (polyvinyl alcohol: polyvinylpyrrolidone=70 wt%:30wt%) was further coated thereon by a bar coater so as to form a dry film thickness of 3 g/m^2, and was dried to form an oxygen-shielding layer, thus preparing a photosensitive lithographic printing plate.

Support-4

The aluminum plate (thickness: 0.24 mm) was degreased with a 3 wt% sodium hydroxide aqueous solution, and was washed with water, and was neutralized by dipping in a 30 wt% sulfuric acid aqueous solution, and was further washed with water. The aluminum plate thus treated was subjected to surface-roughening treatment by hydrolyzing in a 2 wt% nitric acid aqueous solution as an electrolyte at an electric current density of 80 A/dm^2 at 25°C for 11 seconds, and was washed with water, and was subjected to desmut treatment by dipping in a 1 wt% sodium hydroxide aqueous solution at 50°C for 3 seconds, and was then washed with water, and was neutralized by

dipping in a 30 wt% sulfuric acid aqueous solution, and was further washed with water.

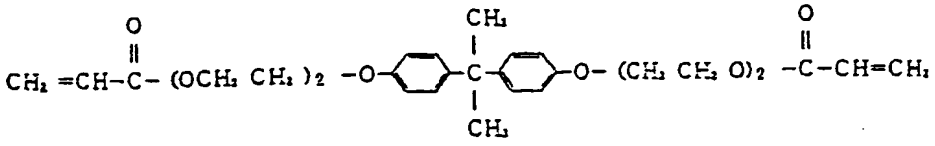
The aluminum plate thus treated was further subjected to anodizing treatment in a 18 wt% sulfuric acid aqueous solution as an electrolyte at an electric current density of 10 A/dm^2 at 30°C to form an anodized film of 23 mg/dm^2, and was washed with water. Thereafter, the aluminum plate thus obtained was dipped in a 0.1 wt% ammonium acetate aqueous solution (pH=9.0) at 85% for 20 seconds, and was treated with a hot water of 90°C for 10 seconds, and was dried to obtain the aluminum plate support having a roughness value Ra=0.60 μm.

(A) Ethylenic unsaturated compound

① Mixture of methacryloyloxyethyl phosphate and bis(methacryloyloxyethyl)phosphate (PM-2 manufactured by Nihon Kayaku K.K. used in Example 1): 11 parts by weight

② Hexamethylenebis[tris(acryloyloxymethyl)-ethylurethane] (UA-306H manufactured by Shin Nakamura Kagaku K.K. used in Example 1): 22 parts by weight

③ 2,2—bis (4 - acryloyloxydiethyleneoxyphenyl) propane of the following formula C: 22 parts by weight



(C)

(B) Photopolymerization initiator

(B-1) Radical generator

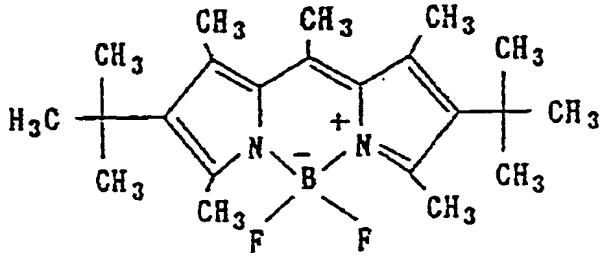
① Dicyclopentadienyltitaniumbis[2,6-difluoro-3-(1-

pyrrolyl)phenyl] (compound of the above formula (B)): 5 parts by weight

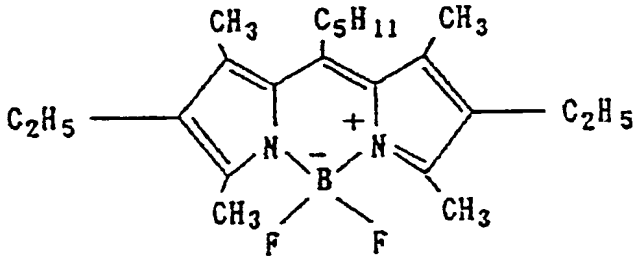
(B-2) Photosensitizer

② Compound of the following formula D: 0.5 part by weight

③ Compound of the following formula E: 0.5 part by weight



(D)



(E)

(B-3) Polymerization accelerator

④ 2-Mercaptobenzothiazole: 5 parts by weight

⑤ N-phenylglycinebenzyl ester: 5 parts by weight

(C) High molecular binder-3

① Reaction product obtained by reacting 3,4-epoxycyclohexylmethyl acrylate with methyl methacrylate (80 mol%)/methacrylic acid (20 mol%) copolymer (weight average molecular weight: 50,000) (acid value= 53, 50 mol% of a carboxyl group of methacrylic acid component

was reacted): 45 parts by weight

Other components

① Pigment (P.B. 15:6): 4 parts by weight

② Dispersing agent ("Disperbyk161" manufactured by Big Chemi Co.): 2 parts by weight

③ Surfactant ("Emulgen104P" manufactured by Kao K.K.): 2 parts by weight

④ Surfactant ("S-381" manufactured by Asahi Glass Company, Limited): 0.3 part by weight

Solvent

① Propylene glycol monomethyl ether acetate: 600 parts by weight

② Cyclohexanone: 545 parts by weight

Each of the above obtained photosensitive lithographic printing plates was subjected to 100% image-exposure by using a FD-YAG laser exposing machine ("Platejet" manufactured by Cymbolic Science International Co.) under conditions of 2000dpi, 6.8 mW (exposure light amount: 120 $\mu J/cm^2$), and was then developed by dipping in a developer comprising 3 wt% of potassium silicate, 5 wt% of sodium alkylnaphthalene sulfonate (concentration: 35 wt%, "Perex NBL" manufactured by Kao K.K.) and 92 wt% of water at 25°C for 30 seconds and by stroking with a sponge one time.

Further, the lithographic printing plate thus treated was subjected to post-exposure treatment under such conditions of post-exposure light source, light

intensity on image-forming surface and temperature on image-forming surface as shown in Table 1, and the lithographic printing plate thus treated was subjected to abrasion test in the following manner to evaluate an image strength, and results are shown in the following Table 3.

A mercury lamp used was H04-L41 manufactured by EYEGRAPHICS Co. (using a gold mirror and a heat ray-cutting filter). An exposure light amount and an exposure light intensity were measured by using UVPZ-1 manufactured by EYEGRAPHICS Co.

A metal halide lamp used was GL-30201BF manufactured by Ushio Denki K.K. An exposure light amount and an exposure light intensity were measured by UV430API (manufactured by Oak Seisakusho).

Abrasion test

Abrasion resistance of an image film was measured by reciprocating a woolen cloth for printing in direct contact with an image-forming surface under a load of 150 g/cm^2 by using an abrasion test machine ("FR-2" manufactured by Suga Shikenki K.K.), and the test results were evaluated by the following evaluation marks.

○: No change is recognized on a film.

△: Abrasion is recognized on a film

×: A film is substantially separated.

Table 3

Table 3

	Metal halide lamp		High pressure mercury lamp		Hot plate heating	Image strength
	Light intensity (mW/cm^2)	Total exposure amount (mJ/cm^2)	Light intensity (mW/cm^2)	Total exposure amount (mJ/cm^2)		
Ex. 4	20	2500	-	-	Done (at 130°C)	○
Ex. 5	80	2500	-	-	Done (at 130°C)	○
Ex. 6	-	-	100	2500	nil	○
Ex. 7	-	-	100	300	nil	○
Comp. Ex. 13	8	2500	-	-	Done (at 130°C)	×
Comp. Ex. 14	13	2500	-	-	Done (at 130°C)	×
Comp. Ex. 15	-	-	13	300	nil	×

As evident from Examples 4 to 7 and Comparative Examples 13 to 15, when a light intensity is high, an image strength is excellent even if the total exposure light amount of post-exposure is the same.

The printing plates obtained in Examples 4 to 7 exhibit a high printing resistance at the time of printing, and particularly Examples 6 and 7 exhibit a remarkably improved printing resistance.

EFFECT OF THE INVENTION

The photosensitive lithographic printing plate of the first feature of the method of the present invention

provides a satisfactory printing resistance before and after storing, and provides a satisfactory stable printing performance without staining.

According to the second feature of the method of the present invention, an image obtained by scanning exposure with laser light provides a satisfactory image strength, and a satisfactory printing resistance at the time of printing. Also, according to the second feature of the method of the present invention, an exposure light amount required by laser exposure can be reduced since a satisfactory image strength can be provided.

CLAIMS:

1. A method for treating a photosensitive lithographic printing plate, which comprises exposing the photosensitive lithographic printing plate to laser light, developing with a developer containing an alkali metal silicate and then carrying out post-exposure treatment, said photosensitive lithographic printing plate being prepared by forming a photopolymerizable photosensitive layer having a film thickness of from 1.2 to 4 g/m^2 and further forming a protective layer having a film thickness of from 2 to 8 g/m^2 on a support having a centerline average height (Ra) of at least 0.35 μm.

2. The method for treating a photosensitive lithographic printing plate according to Claim 1, wherein a mercury lamp is used as a light source for post-exposure.

3. The method for treating a photosensitive lithographic printing plate according to Claim 1, wherein the film thickness of the photopolymerizable photosensitive layer is from 1.2 to 3.5 g/m^2.

4. The method for treating a photosensitive lithographic printing plate according to Claim 1, wherein the film thickness of the protective layer is from 2 to 7 g/m^2.

5. The method for treating a photosensitive lithographic printing plate according to Claim 1, wherein the support is an aluminum support anodized with an

electrolyte containing sulfuric acid.

6. The method for treating a photosensitive lithographic printing plate according to Claim 1, wherein the photopolymerizable photosensitive layer contains at least one (meth)acryloyl group-containing phosphate compound as an ethylenic compound.

7. The method for treating a photosensitive lithographic printing plate according to Claim 1, wherein the photopolymerizable photosensitive layer contains titanocenes as a radical-generating agent.

8. The method for treating a photosensitive lithographic printing plate according to Claim 1, wherein the photopolymerizable photosensitive layer contains a polymer having an ethylenic unsaturated bond on a side chain.

9. A method for treating a photosensitive lithographic printing plate, which comprises exposing the photosensitive lithographic printing plate to laser light, developing and then carrying out post-exposure treatment at a light intensity of at least 20 mW/cm^2 on a surface to be exposed at the time of the post-exposure treatment, said photosensitive lithographic printing plate being prepared by forming a photosensitive layer comprising a photopolymerizable composition containing an ethylenic compound, a photopolymerization initiator and a high molecular binder on the surface of a support.

10. The method for treating a photosensitive

lithographic printing plate according to Claim 9, wherein the light intensity on the surface to be exposed at the time of post-exposure is at least 50 mW/cm^2.

11. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the light intensity on the surface to be exposed at the time of post-exposure is at most 700 mW/cm^2.

12. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the temperature on the surface to be exposed at the time of post-exposure is from 40 to 300°C.

13. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein a mercury lamp is used as a light source for post-exposure.

14. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the ethylenic compound contains a (meth)acryloyloxy group-containing phosphate compound.

15. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the photopolymerization initiator contains titanocenes as a radical-generating agent.

16. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the photopolymerization initiator contains a photosensitizer having an absorption in a visible light

zone.

17. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the high molecular binder contains a polymer having an ethylenic unsaturated bond on a side chain.

18. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the photosensitive lithographic printing plate further has a protective layer formed on the photosensitive layer comprising the photopolymerizable composition.

19. The method for treating a photosensitive lithographic printing plate according to Claim 18, wherein the support has a centerline average height (Ra) of at least 0.35 μm, and the photosensitive layer has a film thickness of from 1.2 to 4 g/m^2, and the protective layer has a film thickness of from 2 to 8 g/m^2.

20. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the developing treatment is carried out by using a developer containing an alkali metal silicate.

21. The method for treating a photosensitive lithographic printing plate according to Claim 9, wherein the developing treatment is carried out by using a developer having a pH value of at most 12.

ABSTRACT

A method for treating a photosensitive lithographic printing plate, which comprises exposing the photosensitive lithographic printing plate to laser light, developing with a developer containing an alkali metal silicate and then carrying out post-exposure treatment, said photosensitive lithographic printing plate being prepared by forming a photopolymerizable photosensitive layer having a film thickness of from 1.2 to 4 g/m^2 and further forming a protective layer having a film thickness of from 2 to 8 g/m^2 on a support having a centerline average height (Ra) of at least 0.35 μm.